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Analytical Chemistry Division Annual Progress Report for Period Ending December 31, 1979

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Introduction and Summary

W. D. Shults, Director

The Analytical Chemistry Division of Oak Ridge National Laboratory (ORNL) is a large and diversified analytical chemistry organization. As such, it serves a multitude of functions for a clientele that exists both in and outside ORNL. These functions fall into the following general categories.

1. **Basic Analytical Research, Development, and Implementation (RD&I).** The division maintains an RD&I program to conceptualize, investigate, develop, assess, improve, and implement advanced technology for chemical and physicochemical measurements. Emphasis is on problems and needs identified with ORNL and Department of Energy (DOE) programs, but attention is also given to needs in the analytical sciences themselves. This program is comprised of medium- to long-term projects and is supported primarily by the DOE. The program constituted approximately 20% of the FY 1979 budget.

2. **Programmatic Research, Development, and Utilization.** The division carries out a wide variety of analytical work that typically involves research and/or development plus the utilization of analytical results or special analytical capabilities to expedite programmatic interests. The effort in this category comes from division, ORNL, and DOE programs and from "Work-for-Others" agreements. Emphasis here is on short- to medium-term projects, depending on the programs themselves. This type of activity accounted for approximately 28% of the division's budget in FY 1979.

3. **Technical Support.** The division performs chemical and physicochemical analyses and tests of virtually all types. Development of methodology is an inherent part of this activity because of the variety of analytical problems that arise in a multiprogram institution like ORNL. In general, this work is short-term in nature and comes largely from other divisions and programs within ORNL; however, a significant fraction originates outside of ORNL. Work that comes from outside of ORNL often involves the use of talent and/or facilities in which the division is particularly strong, unusual, or even unique. This effort accounted for approximately 47% of the budget during FY 1979.

4. **Consultation, Collaboration, and Special Projects.** This work is distinguished from the technical support function by the nature of interaction between the division and its clientele. Work that falls in this category typically requires special attention and/or expertise and hence constitutes a collaborative effort between the "customer" and division personnel. Interactions range from performing highly sophisticated analytical measurements for or with a research staff member, to instructing others in the use of analytical equipment plus the interpretation of data, to participating as analytical members of technical task forces. Activities range from special studies, to program development, to the design and fabrication of analytical instrumentation for others. This work involves close interaction with the staffs of other divisions at ORNL and with non-ORNL people.

Support for this activity comprised approximately 5% of the FY 1979 budget.

The Analytical Chemistry Division is organized into five major sections, each of which may carry out any type of work falling in the four categories mentioned above. Chapters 1 through 5 of this report present progress within the five sections during the period December 1, 1978, to December 31, 1979. The following paragraphs highlight progress in the various sections.

Analytical Methodology Section (Chap. 1). Spectroscopy continues to be prominent in the research effort of the Analytical Instrumentation Group. Work is under way in microspectrophotometry, photoacoustic spectroscopy, resonance ionization spectroscopy, simultaneous multispectral detection techniques, plasma emission (glow discharge) spectroscopy, the use of fiber optic waveguides in analytical spectroscopy, and spectroelectrochemistry. This group is also engaged in the development of in-line monitoring instrumentation for the Consolidated Fuel Reprocessing Program (CFRP) in collaboration with personnel of the Instrumentation and Controls Division.

Study of microgram quantities of compounds of the actinides—their identity, reactivity, thermal properties, and chemical characteristics—is an ongoing collaborative effort with personnel in the Chemistry Division. Microscopic-level spectrophotometry and x-ray diffraction are used as the prime tools. This work entails much more than simply obtaining fundamental spectra; it involves using spectral techniques to elucidate the chemistry of actinide compounds. Emphasis continues to be placed on the chemistry of the halides of einsteinium, berkelium, and californium. We find that oxidation state and crystal structure are preserved in beta decay, and there is evidence that they are preserved in alpha decay also. Our work has expanded this year to include anions other than the halides, and preliminary data suggest that an oxidation state may not be preserved in alpha decay of oxyanion compounds.

There is a natural bond between these studies and the resonance ionization spectroscopy (RIS) research program at ORNL directed by G. S. Hurst of the Health and Safety Research Division. J. P. Young is involved in both programs. Five basic RIS schemes have been devised that could be used to photolytically ionize most of the known elements, and these schemes have been published. Application of RIS to ultra-low-level (radioactive) counting in general, and ^{7}Be counting in particular, is being studied. The latter application is of particular interest because of future solar neutrino counting experiments that are planned. The laser-induced nuclear polarization (LINUP) experiment, led by C. E. Bemis of the Physics Division, was a new activity last year. The LINUP effect was demonstrated with ^{240m}Am this year, and a paper was prepared. These experiments provide the first direct proof and measurement of the large deformations expected for the nucleus of a fission isomer. We also carried out some very preliminary studies of the use of RIS as an element-selective ionization source for mass spectrometry this year.

Pulsed laser-excited photoacoustic (PA) spectroscopy has been under study in this group for several years. This year our work has concentrated on instrument calibration and characterization and on signal generation mechanisms. Additionally, an inexpensive pulsed laser power meter based on a Helmholtz resonator (HR) cell has been developed and tested. We found that the PA signal strength at the wavelength of maximum absorption was linear with weight fraction in studies of holmium oxide mixtures; this is in contrast with reflection spectroscopy data taken on the same set of samples. In the latter case, measured reflectivity is highly nonlinear with weight fraction. We find that PA can be performed with an uncertainty of ±5% for an individual analysis and that the detection limit for holmium oxide is 78 μg for a 30-mg sample.

Acquisition of a commerical laser power meter made it possible to calibrate and study both open cavity and HR cells in terms of PA signal strength for a given input optical energy. We found that the acoustic gain obtained with the HR cell is 10, relative to an open cavity cell, and the background signal improvement is sixfold. Excellent signal linearity is observed as a function of input laser energy. Open cavity cells give waveforms that are highly dependent on both cell geometry and sample. This suggests that several signal generation mechanisms are operative, and we looked into these possibilities. The dominant component of the high-frequency PA signal is due to resonance of the microphone itself in an open cavity cell. Details of our HR cell were published. We completed development of an inexpensive pulsed laser power meter that is based on photoacoustic principles. Advantages of this type of power meter are that it is faster and less subject to thermal drift than conventional photodiode-based power meters. It also provides flat spectral response and does not saturate at high peak powers. The device is quite simple and should cost only about $200.

Last year we mentioned a new technique that we called time-of-flight optical spectroscopy. The project had been initiated through ORNL's exploratory studies program. The idea is to exploit the wavelength dependency of the speed of light through a fiber optic waveguide to separate different wavelengths of light in the time domain. In other words, variations in the transit times of the components of a light pulse can be used to obtain spectral dispersion. Multiwavelength spectroscopy can be performed with a single detector. We have under development two types of fiber optic spectrometers. One uses time-of-flight separation of spectral components; the other uses an array of fibers of different lengths to bring the spatially dispersed output of a grating spectrometer to a single detector, in sequence. Our time-of-flight spectrometer has been developed in the dual-beam mode, in which two optical fibers of slightly different lengths are used, one for the sample and one for the reference cell. Because one fiber is longer than the other, the sample and reference spectra have different transit times and can be measured sequentially. The second type of spectrometer uses several fibers of different lengths to multiplex a number of simultaneous pulses of different wavelengths onto a single photomultiplier detector. The initial version of this device uses an array of 30 fibers of lengths ranging from 1 to 59 m. This gives a time delay of approximately 10 ns between successive fiber channels. This configuration gives a 90-nm coverage, which can be utilized anywhere within the range of the grating monochromator. Much of this work has been published, and part was presented at the Gordon Research Conference of Analytical Chemistry.

A new activity this year is time-resolved laser spectroscopy. We have acquired a mode-locked argon ion laser that can be used to emit optical pulses with durations of approximately 100 ps and repetition rates of about 100 MHz. Optical components and electronic detection equipment have been acquired and/or constructed. A high-speed photodiode, with a rise time of less than 50 ps, was constructed. This system, when complete, should have many desirable characteristics for time-resolved spectroscopy, and we plan to use it for studies of analytical problems of various types.

During the past year, studies of the use of rapid scan spectrometry for liquid chromatographic detection were completed. We have now begun to use that technique for spectroelectrochemical studies. The particular chemical system of interest is the oxidation and reduction of sulfur species in chloraluminate melts ($AlCl_3$-NaCl mixtures). Two types of optically transparent electrodes are used, platinum screens and thin slices of glassy carbon foam. The work to date has emphasized the characterization of the positive oxidation states of sulfur in acidic melts.

We completed a theoretical study of the geometrical and spatial aspects of flame atomic absorption spectroscopic (FAAS) experiments. This study indicates that some common experimental problems in FAAS could be circumvented by designing a burner that matches the optical beam profile. Work aimed at using our glow discharge detection (GDD) scheme for determining fluoride at trace levels has continued. Two approaches have been studied.

One involves the release of volatile inorganic fluorides via a small platinum furnace located a short distance from the GDD. The second involves formation and extraction (for GDD measurement) of organic silyl compounds that contain fluoride. We can detect 10^{-10} g of fluoride by the latter technique; these results are now being compared with those obtained by the platinum furnace approach.

A second major category of work that takes place in the Analytical Instrumentation Group is research into and development of specialized instrumentation. Last year we mentioned the development of in-line sensors for the CFRP. Our role is to conceptualize and demonstrate feasibility; the Instrumentation and Controls Division then develops the needed hardware and software. Much progress has been made during this period. Our dual wavelength uranium monitor has been completed through the engineering stage. The prototype is currently being evaluated; it monitors uranium in the 20 to 200 g/liter range in aqueous media of low- or high-acid concentration. Determination of uranium in tri-n-butylphosphate (TBP) solutions is being studied. Work with the free nitric acid monitor is also complete. The procedure has been published, a patent has been applied for, and a prototype is being evaluated. Currently, we are investigating a dual wavelength spectrophotometric approach for measuring plutonium solutions. We studied the utility of electrochemical techniques for measuring plutonium oxidation states as well as total plutonium.

During this year significant progress has been made within a new project that is directed at developing state-of-the-art analytical hot-cell instrumentation. A TBP analyzer, based on the measurement of dielectric constant, was developed and put into operation. It measures TBP in *n*-dodecane within the 0 to 35% range in 5 min, with errors of 0.1% or less. This work has been submitted for publication. Several different minicomputers and microprocessors were evaluated for incorporation into hot-cell instrumentation. We are currently developing both a computer-controlled pipetter and a titrator and are planning for development of spectrophotometric instrumentation specifically for hot-cell use.

The Physicochemical Analysis Group carries out a variety of rather specialized nonroutine service and development projects at ORNL and maintains a long-range research program. During this period, the group completed the study (first reported last year) of chemical characteristics of ponded ash. Along with personnel in the Chemistry Division, they have studied the passivation of titanium electrodes, using electron spectrometry. Similar work involves the study of nickel cathodes used as electron guns in ORELA; the objective is the optimization of their performance. This group was asked this [illegible] to develop a method for measuring asbestos which could be used to ensure that the asbestos content of various building materials is less than 1%. Our monochromated x-ray diffraction system, reported last year, was used to do this. Gypsum is a common component (and interference) in this type of measurement, but we determined that simply heating the sample at 300°C is a convenient way to remove gypsum interference. We are preparing this asbestos study for publication.

The highlight of the research effort in this group during the current year has been the work with positron spectroscopy, which was supported initially by ORNL's exploratory studies ("seed-money") program. Most of the effort has been devoted to development of a positron source that can be used for spectrometric experiments. S. Pendyala, from the State University of New York at Fredonia, has been a close collaborator in this project. S. Pendyala, John Dale, and Lester Hulett have found that carefully prepared tungsten and molybdenum moderators can be used to produce monoenergetic positrons that have an intrinsic FWHM less than 1 eV. The yields using tungsten and molybdenum were 100 times greater than those of common moderators such as magnesium oxide. We have purchased a high-intensity ^{22}Na source of positrons and hope to prepare a practical positron gun with it, such that we can proceed to investigate positron spectroscopy as a surface analysis tool. The ORNL-built electrostatic electron spectrometer is being used for this work.

Mass and Emission Spectrometry Section (Chap. 2). The Mass and Emission Spectrometry Section is comprised of four groups: actinides and inorganic mass spectrometry, elemental and ion probe spectroscopy, organic mass spectrometry, and research and development and safeguards mass spectrometry. Both research and development and technical support are carried out within each of these groups.

Research into the ion chemistry $C_7H_7O^+$ has continued. This is an important secondary ion in the mass spectra of many oxygen-containing aromatic compounds. The metastable kinetic energy release and relative branching ratios for loss of CO and CH_2O from decomposing $C_7H_7O^+$ ions are consistent with four distinct structures. The objective of these studies is to gain a better understanding of the effects of structural configuration on organic mass spectra. We are currently concluding experiments that will enable us to prepare this work for publication.

A highlight in the Organic Mass Spectroscopy Group this year has been the design, construction, and performance evaluation of a three-sector mass spectrometer. This was mentioned very briefly in the last annual report as a potential modification of our double-focusing instrument. A second electric sector was added to the original instrument and is of the same design as electric sector I. A unique feature of this three-sector configuration is that the double-focusing components (electric sector I plus magnet) can be operated in high-resolution mode, and metastable spectra of mass separated components obtained by electric sector II. This type of experiment is analogous to capillary column gas chromatography mass spectrometry in that a high-resolution separation device precedes mass spectrometric identification. In this case, a high-resolution mass spectrometer comprises the separation device. We have successfully demonstrated this mode of operation, using a resolving power of about 14,000. A complete description of our instrument is being published. We have also carried out initial experiments into photofragmentation spectrometry (PFS) with the three-sector instrument. In this mode, the ion of interest is mass selected by the double-focusing components, and a photon beam is used to activate and fragment ions in the third field-free region so that they can be analyzed via conventional ion kinetic energy scans. In this case, the second electric sector is a kinetic energy analyzer calibrated in mass units. Further work in PFS is planned.

We are engaged in an EPA-sponsored project in which air samples are taken from an industrialized area near the Gulf of Mexico and analyzed extensively for organic constituents. The primary purposes of this study have been to furnish baseline data on identifiable pollutants, to assess state-of-the-art techniques, and to assess the quality assurance plan that is proposed for such projects. We are one of three laboratories involved in this multiyear study. We completed data acquisition from all samples this year and are now proceeding with data processing. Approximately 150 components have been identified in these samples; major components were aliphatic and aromatic hydrocarbons. Interlaboratory comparison of data from one study area gave about 85% agreement in compound identification, which is very satisfactory, considering the differences in instrumentation and techniques used by the three participating laboratories. In addition to this massive organic analysis program, the Organic Mass Spectrometry Group has given support to a wide variety of programs within ORNL and the other Nuclear Division operations during this period.

Recently, some exploratory studies were made to evaluate the potential of our ion microprobe mass spectrometer (IMMA) for mass spectral studies of nonvolatile organic and/or organometallic substances. The ion microprobe is attractive for this type of study because it has high sensitivity, it has the ability to select a variety of ionizing reagents, and the primary ion energy can be controlled. We observed an abundant secondary ion current that corresponded to cationized organic species and fragmentation of the cationized organic substrate. Additional experiments are planned to test fragmentation schemes observed in these preliminary experiments.

Secondary ion mass spectrometry (SIMS) allows one to perform mass and isotopic analysis on samples that are sometimes not amenable to other mass spectrometric techniques. The advantage here is that difficult chemical preparation steps may be circumvented. This year we developed methods that allow the use of SIMS for the rapid and accurate determination of lithium and boron isotopic ratios in difficult sample types. Several immediate applications of this important measurement have been made, not the least of which was the analysis of samples from Three Mile Island (TMI).

The duoplasmatron source used to generate the primary ion beam for IMMA produces satisfactory yields of secondary positive ions for electropositive elements but has reduced sensitivity for most of the electronegative elements. Bombardment with cesium ions is useful for producing negative secondary ions, because cesium lowers the work function at the surface of a sample, thereby increasing the availability of electrons and fostering high yields of negative secondary ions, and eliminates oxygen-containing species. We have developed a cesium ion source that is interchangeable with the present duoplasmatron source in our IMMA. Several sources were studied, and we are continuing development to improve beam intensity. We have been able to carry out some depth-profiling experiments with arsenic and phosphorous implanted in silicon. Sensitivity for arsenic was increased by a factor of 10 over that obtained when an O_2^+ beam was used. We expect the cesium ion source to have unique applications for depth profiling of *n*-type implanted dopants.

For several years now we have worked with personnel in the Chemistry Division in a study of the effect of oxide formation on Incoloy-800 tubes as barriers to tritium permeation. To facilitate these studies, we had to develop a quantitative SIMS technique that is applicable to both nickel- and iron-based alloys. The method involves using matrix ion species to index empirical sensitivity factors. This method, when applied to the above-mentioned oxide films, provides significant improvement in analytical accuracy as compared to single-sensitivity factor techniques. An outgrowth of these studies on oxide composition has been some initial experiments with laser annealed samples. Considerable differences exist between oxidized surfaces outside and inside a laser annealed region, whether or not the oxidation is light or heavy. This investigation is intended to determine whether or not laser annealing will be a beneficial surface modification technique for controlling tritium permeation behavior.

The ability to deliver a precisely known dose in a known concentration profile makes ion implantation an excellent method for preparing surface analytical standards. The method is completely general in that any element can be implanted into a properly prepared surface of almost any material. We prepared implantation standards of ^{11}B at three different concentration levels on a polished Zircaloy-2 surface. We were then able to show that ion implantation standards can be used effectively to calibrate a spark source mass spectrometer (SSMS) for near-surface analysis. Precise control of sparking conditions in the SSMS provides the basis for calibrating the SSMS for near-surface region analytical studies. This work has been published.

We have begun to carry out some fundamental studies in SSMS techniques, with the objective of improving the precision of this type of analysis. A servocontroller was developed to maintain the spark gap width at a constant value, because gap width is ordinarily an uncontrolled parameter that leads to loss of analytical precision. The controller that we developed not only provides a constant gap width and hence improved precision but also has proved to be useful for long exposures, which usually require close operator intervention.

We are also using a fast beam chopper in conjuction with the gap controller. This allows a more controlled portion of the spark pulse to be sampled and reduces inhomogeneous effects. Results of analyses are now being monitored to compare the precision measured with these alterations in operation and the precision obtained with an unaltered mass spectrometer.

Much progress has been made toward establishing SSMS capabilities for highly radioactive materials. A surplus instrument was acquired and has now been fully tested and prepared for installation in our hot-cell laboratories in Building 2026. The shielded cubicle and transfer system has been designed, and construction is well under way. We expect to complete this unique facility within the year; it should be capable of handling solid samples that read 40 $\mathrm{R\ h^{-1}}$ at 1 cm.

Evaluation of the channel electron multiplier array detector (CEMA) for SSMS was completed this year. Several optical detectors were tested as part of this study, and quantitative data were obtained on three types of samples to assess the system's versatility and potential. Our results show that improvements in dynamic range and spatial resolution of the CEMA are required before it will supplant photoplates or multipliers. Two publications of this work have been submitted. This work was part of D. L. Donohue's Ph.D. thesis research.

We have continued to develop and apply the resin bead technique of sample preparation for isotopic characterization and isotope dilution quantitation analysis by mass spectrometry. This technique was extremely useful in our work with TMI samples of various types. Minor isotopes in the 1% concentration range can be measured with precision of ±0.5%, and major isotopes in the 50 to 99% range can be measured with precision of ±0.1% by this technique. A tentative method for the determination of thorium has been developed and evaluated on "cold" synthetic standards and samples using ^{230}Th as tracer for the isotope dilution measurement. The development of an isotope dilution method for ^{99}Tc has also been completed this year. This method employs resin bead loading and ^{97}Tc as the isotope spike; the limit of detection is 0.1 to 0.2 pg. This work was done in collaboration with members of the Nuclear and Radiochemical Analysis Section. We continue efforts to demonstrate the utility of the resin bead sample-loading technique as a viable analytical tool for measuring uranium and plutonium for safeguarding purposes. This year demonstration of the compatibility of this sample-loading technique with single-stage mass spectrometric measurements was completed. We have ordered a quadrupole mass spectrometer and will assess its utility as an onsite analytical instrument. We are systematically trying to improve the precision, which is routinely available by the resin bead technique, as we teach others how to use it and assist in its implementation on a national and international basis. Because of this work and other applications that utilize high-abundance sensitivity mass spectrometry, a program of modernization for the electronics systems of our mass spectrometers has been initiated. It is interesting to note that samples of americium, curium, and californium are now routinely submitted to us on resin beads for isotopic analysis. This results in the handling and transferring of much smaller amounts of highly radioactive material, while yielding more reliable analytical results.

Technical Support Section (Chap. 3). Each of the groups in this section must cope with a wide variety of analytical problems and special projects. Characteristically, they must also participate in collaborative studies with members of other divisions and programs at ORNL. An important function is that we maintain an awareness of new developments in analytical technology and adopt them quickly, when appropriate. This year a time-of-flight mass spectrometry system was set up for pyrolytic studies in support of reactor programs. Coupled with this are thermal analysis capabilities (including differential thermal analysis), differential scanning calorimetry, and thermogravimetric analysis. A computer-based system for making BET measurements in both the adsorption or desorption mode has been designed and constructed. It utilizes a Hewlett-Packard 9835 computer for control and data acquisition and for display purposes. We now have surface area measurement capabilities that are based upon either pressure or weight changes. Our Technicon analyzer capabilities were upgraded this year, and we completed construction of a shielded and contained spectrophotometry system in the hot-cell area of Building 3019. This facility will enable us to measure high-quality spectra on highly radioactive samples of all types. It will utilize a Cary Model 14H spectrophotometer as the core instrument.

We undertook a program of renovation in our hot-cell facilities this year and have expended considerable effort upgrading the cell windows, boxes, and conveyers. This renovation parallels the development of microprocessor-based instrumentation for hot-cell operations in the Analytical Instrumentation Group. Concurrently, we have evaluated the performance of a Mettler Titrator, acquired a Parr density meter, and studied the use of fiber optics for spectrophotometry within the hot cells. The division's new x-ray fluorescence system has been installed and placed in operation. It is designed to facilitate analysis of both nonradioactive and radioactive materials, utilizing several different x-ray sources and detectors. The prime user will be the CFRP, but it will be available for other activities as well. Currently, we are training operators to take full advantage of this elaborate system.

We evaluated the Davies and Gray procedure for high-precision analysis of uranium by studying its use with hot-dissolver solutions and published the results. Ion chromatography was used to develop a method for measuring dibutyl phosphate, and high-pressure liquid chromatography (HPLC) has been used to study the use of phenacyl- and naphthacyl-derivatives of mono- and dialkyl phosphoric acids. These ultraviolet-sensitive chromophores provide enhanced sensitivity over gas chromatographic methods for determining these important acids. These projects were carried out within the Reactor Programs Group, which continues to work within various nuclear reactor programs at ORNL and serves as liaison between the programs and the division. Various components of work done for these programs are reported in the activities of the respective sections.

Another activity that warrants mention is our testing program for nuclear coatings (paints). We maintain capabilities to perform the three major tests: decontamination factor, radiation resistance, and simulated loss of coolant accident. During this reporting period, 1400 steel panel and concrete block specimens were examined for 14 manufacturers and nuclear utility companies.

The division was called upon to provide a great deal of analytical support related to the TMI incident this year. That work was carried out in several sections of the division, with the Technical Support Section responsible for receiving and dispensing samples to the appropriate laboratories and for providing specialized analyses of various types. The Nuclear and Radiochemistry and the Mass Spectrometry sections have been prominent in the TMI effort. TMI has been a demanding, but truly exciting, intradivisional activity.

Bio-Organic Analysis Section (Chap. 4). The work of the Bio-Organic Analysis Section is programmatic in nature, with strong emphasis on programs related to health and the environment. This section develops and provides methodolgy, materials, and hardware for biological and environmental studies, plus data to support these studies. There are three groups: one emphasizes quantitative analysis, a second emphasizes isolations and identification, and the third conducts a variety of special projects and programs. Considerable overlay of technical interests exists between these groups and with other sections in the division. Because of the programmatic nature of this work, much of the effort here is directed to acquiring information as opposed to just collecting data. Two divisional programs — the Life Sciences Synthetic Fuels Program and the Tobacco Smoke Chemistry Program — exist within this section, although their work cuts across several sections.

The Quantitative Methods and Applications Group has an abiding interest in the determination of benzo(*a*)pyrene (BaP), because BaP content is often used as an estimate of carcinogenicity. Its presence and levels in synthetic crude oils and fuels are especially important. The reliability of the methods that are used for BaP analysis has been a concern, because the procedures are based on assumptions that have not been adequately validated in the past. We addressed this issue this year, using ^{14}C-labeled BaP tracer, so that overall recoveries could be monitored. Basically, we developed and evaluated two separations procedures that provide 60 to 80% recovery of BaP: one requires 10 d and the other requires 3 d. The final measurement can then be made by fluorescence or gas or liquid chromatography. We used a coal gasifier tar, a coal liquefaction product, a crude shale oil, a petroleum crude, and a diesel fuel for evaluating these procedures. Although a statistically significant difference exists between results obtained using the two isolation methods, the discrepancy is easily within limits of uncertainty for our complex mixtures and trace levels. We are now routinely employing the abbreviated procedure and two of the three analytical measurement methods to determine BaP content of a variety of petroleum substitutes.

The sampling and analysis of vapor phase organic compounds continues to be of interest to many programs. During this reporting period, we have refined previously reported procedures for vapor phase organics to improve repeatability as well as quantitation. We selected 1, 2, 4-trichlorobenzene as the internal standard for this type of measurement. Samples are collected on Tenax, thermally desorbed onto a glass capillary column held at -70°C, and then eluted with the temperature programmed to 160°C. Flame ionization detection is used. This procedure is capable of measuring at least 100 vapor phase organics with boiling points between 40 and 250°C. A wide range of paraffins and aromatics can be distinguished, including some of the common, difficult-to-separate isomers. This procedure has been utilized for samples collected by the EPA during their Yugoslavian gasifier study and for examination of head-space volatiles.

Previous work for the Electric Power Research Institute suggested that sorption of polynuclear aromatic hydrocarbons (PAHs) on fly ash is selective for aromatic compounds and is inversely related to the size of the PAH ring system. More importantly five-ring PAHs (such as BaP) are difficult to extract from fly ash, yielding recoveries of less than 30% at times. Procedures are needed to assure reproducible and known extraction behavior if accurate results are to be obtained. This year we have begun studies to quantitatively characterize this sorption. Using ^{14}C-labeled BaP, we have established that the BaP distributes between fly ash and the solvent—it is not lost on glassware and other surfaces. This work can provide more than improved procedures; it can also provide better understanding of the bioaccessibility of PAHs on particulates.

During this reporting period, we expanded our capabilities in HPLC and have added Fourier transform infrared capabilities. Physical facilities for storing as much as barrel quantities of research samples were established this year; there are now approximately 200 different sample types in the repository. Four representative materials are undergoing thorough characterization and study, with respect to stability over the long term.

The Isolation and Identifications Group has continued to address the very important question of mutagenic constituents in synfuels. We have been concerned with components of the basic and neutral fractions primarily, because short-term mutagenesis assays (Ames) have consistently shown that these are most mutagenic. The basic fraction is defined as that which partitions into the ether phase of an aqueous-ether solvent distribution system after removal of neutrals in a preceding step. This ether soluble base (ESB) fraction constitutes 1 to 10 wt % of the synfuel materials that have been fractionated. We have developed a subfractionation scheme that is tailored to isolate mutagenic components of the ESB. The mutagenic bases are characterized by fused-ring systems incorporating one nitrogen atom within the molecule and having appreciable alkyl-substitution. The most active compounds are found to be primary amino-substituted PAHs. Derivatization was used to distinguish the types of compounds. Currently, we are trying to identify the structural features of the major components, using chemistry, spectroscopy, and chemical synthesis as prime tools.

The mutagenic components of the neutral fraction of synfuels have not been studied to the same extent as have those of the basic fraction. Last year we reported studies of the multialkylated PAHs and their contribution to overall mutagenesis of the neutral fraction. This year we have examined the neutral nitrogen compounds that accompany PAHs in subfractionation of neutral components, and we are currently examining their contribution to mutagenicity. The neutral nitrogen compounds are concentrated with PAH isolates and comprise 1 to 10% of the PAH subfraction. New nuclear magnetic resonance instrumentation was acquired this year and is proving to be especially useful for screening these synfuel extracts.

The extensive experience with separation and identification procedures in this section is beginning to be utilized in engineering and materials science programs related to fossil energy technology. Projects of this nature are carried in collaboration with other divisions at ORNL. As one example, we are currently collaborating with personnel of the Metals and Ceramics Division in an investigation of the causes of high rates of corrosion that are encountered in some coal conversion pilot plants.

The use of liquid crystal stationary phases for glass capillary gas chromatography was investigated this year by the Special Projects Group. It was necessary to study column preparation techniques and column performance as part of this study. We did so and are now able to separate geometric isomers that had not been resolvable by other means. Glass capillary column technology is under continual study in this group for general use within the Laboratory. We discovered that the use of trimethylchlorosilane (TMCS) as a catalyst in preparing glass columns has been an unknown source of problems in the past. By eliminating TMCS in the column preparation procedures, the thermal limits of stationary phases have been extended significantly. For example, Dexsil-400 columns can be used up to 375°C (rather than 320°C) if prepared properly, and concurrently, column lifetime is improved.

Our Tobacco Smoke Chemistry Program falls organizationally within the Special Projects Group. This program continues to provide routine and nonroutine analytical support plus R&D to the National Cancer Institute and several of its contractors. Last year we reported the determination of nicotine in physiological fluids, blood and urine, as an attractive means for measuring the dose to a given smoker. This has been a collaborative study with Borriston Research Laboratories (BRL) in which dogs are exposed to cigarette smoke that contained ^{14}C-nicotine. That work has continued. Results to date indicate that, as a group, the animals (beagle dogs) retain about 20% of the smoke particulates that are made available for inhalation. On an individual animal basis, there appears to be very little correlation between levels of nicotine in the urine and smoke deposition in the lungs. Accordingly, we have begun to examine the feasibility of using carbon monoxide (CO) in exhaled breath as a potential chemical dosimeter. Preliminary experiments with beagles at BRL indicate that carbon monoxide concentrations in exhaled breath are roughly proportional to blood carboxyhemoglobin levels. Initial information also indicates that human nonsmokers have concentrations in their breath of 2 to 5 ppm carbon monoxide, whereas smokers have breath concentrations of 25 to 45 ppm carbon monoxide.

Carbon monoxide is one of the parameters that we measured—along with "tar" and nicotine—for the U.S. Department of Health, Education, and Welfare. By special request, more than 120 popular brands of commercial cigarettes were surveyed to support the Surgeon General's report on smoking and health. The carbon monoxide delivery per cigarette ranged from 1 to 29 mg in the brands analyzed. The Federal Trade Commission is presently developing an automated procedure for the determination of carbon monoxide and is using our data as a standard for comparison with its initial results. Designation of carbon monoxide deliveries, in a manner similar to that now required for "tar" and nicotine, may soon be required in cigarette advertising.

Last year we reported studies of the chemiluminescence technique for determining NO, NO_2, and NO_x in tobacco smoke. At that time, we were finding larger-than-expected proportions of NO_2 in the oxides of nitrogen. During this year, we have established that the apparent high level of NO_2 was really an artifact of the aging of the smoke puffs themselves within the smoking machine. Aging permits NO to be converted to NO_2 by reaction with oxygen in the smoke. However, our work continues to confirm that the concentration of NO ($\approx NO_x$) in cigarette smoke is considerably larger (by 50 to 100%) than that determined by other analytical methods. This has led to closer scrutiny of procedures that are used by other laboratories.

One other new project warrants mention. The Department of Defense has asked that we chemically and physically characterize aerosols that are analogous to "smoke screens" and help produce them for biological testing. To do this, we have set up within one of our laboratories a surrogate "smoke screen" generator. We will be comparing the smoke generated by this system with that generated by an M-60 battle tank and characterizing the aerosol chamber environment during biological studies.

Nuclear and Radiochemical Analysis Section (Chap. 5). This has been a year of growth for the Nuclear and Radiochemical Analysis Section—growth in work output, efficiency, facilities, and quality assurance. The formal organization of the group comprises a Low-Level Radiochemical Analysis Group, a Radiochemical and Activation Analysis Group, and a Special Projects Group. All three groups perform work that ranges from routine radiochemical analysis to short-term development projects. Long-term development and research are carried out primarily in the special projects group.

New laboratories and a counting room were put into full operation during this reporting period by the Low-Level Radiochemical Analysis Group. The new Nuclear Data (ND) 6603 spectrometer system mentioned last year is now fully operational and has taken over the workload formerly handled by an ND-3300 system. It presently uses five surface barrier alpha detectors and three new high-efficiency germanium detectors. We plan to add four additional alpha detectors and perhaps three sodium iodide detectors to this system in the future. The work of this group primarily comprises analytical support for such activities as the Clinch River actinides program, the waste management program, the ORNL waste treatment plant operations, environmental surveillance, and fallout monitoring. Approximately 25% of the analytical effort in the Low-Level Radiochemical Analysis Group is committed to the analysis of statutory samples.

The Radiochemical and Activation Analysis Group also performs a variety of analyses for ORNL and Nuclear Division programs. A major effort was undertaken this year to implement the full power of the ND-6620 computer-based data acquisition system. The objective was to minimize manual processing. Programs have been written to improve data acquisition, to dynamically allocate system resources, and to perform data analysis for virtually every gamma ray spectrometric analysis performed in this group. Software has also been developed to allow use of the ND-6620 system for batch processing after regular working hours. This effort now provides a very powerful analytical system tailored for the exact needs of the user; it is flexible, reliable, and well-integrated into this laboratory environment. The demand for multielement and uranium analyses increased by 35% in this laboratory during the last year.

A new project this year, sponsored by IBM, involves the development and use of methods for measuring uranium and thorium impurities in pure silicon at the 1- to 2-ppb level. These impurities can lead to so-called soft errors in random access memories. Another new project that should be mentioned is the study of trace elements in human lungs, which is being done by Prof. Gail Norris, while on sabbatical leave with this section. We have made significant improvements in the separation scheme for ^{14}C from reactor fuel solutions, gaining a decrease in analysis time from 2 h to 20 min. This improved gas train has been placed in routine use, and the work is being published as an ORNL report.

The applicability of Cerenkov counting was evaluated for measurement of low-level beta radioactivity, with particular reference to the ^{90}Y daughter of ^{90}Sr. After optimization of our system, we obtained a minimum detectable activity of ^{90}Y for a 100-min count of about 1.5 Bq. We demonstrated the usefulness of Cerenkov counting for direct screening of water samples and reported our work in a paper at the International Conference on Liquid Scintillation Counting. Currently, we are developing chemical separation schemes to concentrate strontium and yttrium from large aqueous volumes, to remove interfering radionuclides, and to eliminate colored substances that may cause quenching. We expect to use Cerenkov counting for analysis of samples on a routine basis in the near future. Members of the Special Projects Group are also involved in a number of collaborative projects with members of other divisions at the Laboratory. These include characterization of species and sources at a solid waste disposal site, investigation of radionuclide concentrations in water and sediment as a function of flow in White Oak Creek, and measurement of specific radionuclide concentrations in air monitoring samples from the Laboratory environs.

A major activity within this section has been directed at the analysis of technetium. We have developed procedures for separating and determining ^{99}Tc by beta counting at the 1 pCi level, ~0.06 ng. We have also developed a method for determining ^{99}Tc by neutron activation analysis to be applied to fission product solutions. The method has been in routine use now for eight months. The sensitivity of the analysis is approximately 5 ng, and samples of up to 100-ml volume are easily processed. This procedure is being published. Finally, we have collaborated with the Mass and Emission Spectrometry Section in developing an isotope dilution mass spectrometric method for final measurement of low levels of technetium. To develop that procedure, enriched ^{97}Tc had to be prepared by irradiation of a ^{96}Ru target. In doing so, we found a surprisingly high content of ^{98}Tc and ^{99}Tc. Arrangements are now under way to irradiate a small portion of the technetium product under well-defined flux conditions so that we can determine the n,γ cross sections of these isotopes. These cross-section data are not now available.

The highlight of the year, insofar as the Nuclear and Radiochemical Analysis Section goes, has been our involvement in analysis related to the TMI incident. Members of this section participated onsite in initial stages of the accident investigation and have been called on to provide many and varied analyses for radionuclides in support of work going on at the Laboratory and elsewhere relative to the accident. Other sections in the division also participated in this activity. In total, some twelve staff members received special citations from the DOE for their efforts in support of the analysis of the TMI incident.

Chapters 6 and 7 contain information that reflects the work of the division as a unit. Information about the quality assurance and safety programs is presented in Chap. 6, along with the tabulation of analyses rendered. Publications, oral presentations, professional activities, educational programs, and seminars are cited in Chaps. 7 and 8. Approximately 132 articles and reports have been published, including entries in seven books, and 129 oral presentations were given during this reporting period.

1. Analytical Methodology

W. S. Lyon. Section Head

This section of the Analytical Chemistry Division is divided into two groups: Analytical Instrumentation and Physicochemical Analysis. Both groups perform basic and applied research; in addition, the latter group does some special analysis.

Applied work in Analytical Instrumentation this year has included an accelerated effort to improve instrumentation for hot cells within the Division, in-line sensor development for the Consolidated Fuel Reprocessing Program (CFRP), and electrochemical studies related to use of batteries, fuel cells, and catalysis. The hot-cell instrumentation has three key concepts: stand-alone operation, closed-loop control, and flexibility. Instruments or systems studied under the CFRP in-line sensor program this year have included free-acid monitor, electrochemical in-line sensors, and a uranium monitor. Spectrochemical studies have been concerned mainly with oxidation states and the chemistry of sulfur. In the more basic work, resonance ionization spectroscopy continues to be studied and used in a number of cooperative research projects. Photoacoustic studies have concentrated on instrument calibration and characterization and on signal generation. Also an inexpensive pulsed laser power meter was built. Fiber optic waveguides are under development for use in spectrometers; one type uses wavelength dispersion, and the other uses an array of different length filters. A new project, time-resolved laser spectroscopy, was initiated. The spectrophotometric studies on transuranium compounds have continued, as has the development of flame emission methods for halogens. Theoretical calculations in flame atomic absorption spectrometry have been made in an effort to optimize parameters for this technique.

In the Physicochemical Analysis group, x-ray photoelectron spectroscopy is being used in a number of surface studies, most of which are interdivisional. Improvements have been made to both the electrostatic and the magnetic spectrometer, but baseline shifts continue to be a problem. Additional interdivisional projects, using transmission and scanning electron microscopy, involve such diverse problems as the nickel cathode surfaces of the ORELA electron gun, sorption of metal ions in natural waters on manganese dioxide surfaces, characterization of coal and fly ash, corrosion scale from a liquid potassium heat exchanger, and studies of molten-salt processes related to battery and fuel-cell design. A 90-position automatic sample changer has been added to the x-ray fluorescence (XRF) unit in Building 4500N. The system has been used for a variety of different samples. In addition, a new XRF unit for use in our hot-cell laboratories has been purchased, installed, and is now in use. This system has both SiLi and germanium detectors, and excitation is provided by an x-ray tube or one of three radioactive sources (^{109}Cd, ^{241}Am, ^{57}Co). X-ray diffraction is another important analytical tool in the Physicochemical Analysis group; the structure of a number of research compounds has been elucidated with it, and a technique has been developed to monitor EPA-defined limits of asbestos in building materials. Two interesting research projects are (1) chemical speciation of fly ash from coal-burning power plants and (2) positron spectroscopy. The former was brought to a conclusion this year; the latter is continuing. Both are fundamental in nature but of great applicability. The fly-ash speciation work has resulted in a new concept of how elements are incorporated in fly ash. Three phases of fly ash have been described: glassy, crystal and magnetic. Each has an enrichment of certain particular elements. Positron spectroscopy opens the possibility of a new surface analysis technique that could be applied to many problems. To summarize, this has been a productive and exciting year for the section.

ANALYTICAL INSTRUMENTATION

H. H. Ross, Group Leader

Advanced Instrumentation

Remote instrumentation development. A new project designed to meet the instrumentation requirements associated with the analysis of highly radioactive samples and other unique instrumentation needs of the Analytical Chemistry Division was initiated during this reporting period. An assessment of the needs, the development of a general project plan, and the procurement of key pieces of equipment were major objectives this year.

Current instrumentation for the hot-cell analytical laboratories dates from the mid-1950s. The electronic systems still utilize vacuum tube technology and, because the original mechanical subunits employ numerous components that are no longer available, maintenance has become a severe problem. The lack of development activity during the last two decades has greatly limited the analytical capabilities. Support of the nuclear fuel reprocessing research and development programs requires an expanded analytical methodology capability, as well as an improved system for documenting the work performed within these laboratories.

The general project plan embodies several key concepts. First, each instrument must be capable of stand-alone operation. Second, each instrument will employ a closed-loop control concept, thereby reducing the number of remote manipulator operations and increasing the reliability of operation. Third, the capability to correct, or at least record, operator actions is required. The final element of the general project plan is flexibility; that is, the instruments must possess features that allow them to be adapted quickly to new applications and at minimum cost.

These key concepts can be realized through use of a microcomputer-based controller. The closed-loop control function is defined by the program; varying the control function, thus changing the analytical application, is accomplished via changes in the program rather than by the redesign of the hardware. The ability to record operator actions and to communicate with a central data management system are inherent in a microcomputer-based controller. The low cost of microcomputer systems equipped with a high-level language programming capability, such as BASIC, allow one to achieve stand-alone operation and redundancy of electronic modules among a variety of instruments. Funds to purchase candidate microcomputer systems were acquired, and the delivery of the last system is scheduled for the immediate future.

Defining a control function in software means one must perform calculations concurrent with the control operation. Execution time of the programming language is an important criterion. Benchmark programs, selected to be representative of anticipated calculations, were executed on a Digital Equipment Corporation LSI-11 equipped with a hardware floating-point processor, a Digital Equipment Corporation PDP-8, and a Rockwell AIM 65 system. The LSI-11 exhibited the shortest execution time but only 50% shorter than the AIM 65, which performs all floating-point operations via software routines. Comparative execution times of the PDP-8 varied significantly with the type of calculation and yielded times comparable to those obtained with the AIM 65 and as much as 2.7 times longer. The AIM 65 system costs $700, and the LSI-11 system costs $6600.

Instrument development activity has focused upon a new remote pipetting system and a laboratory instrument to measure tri-*n*-butylphosphate (TBP) in hydrocarbon mixtures. The instrument designed to measure TBP measures the dielectric constant of the solution and is based on the circuit concept utilized in a dielectric constant liquid chromatography detector developed by Klatt.[1] The resonant frequency of a tuned network containing the detector cell as the capacitive element is related to the volume fraction of TBP in the sample. Because dielectric constant is a bulk property, chemical pretreatment of the sample is required to remove interferences. The observed frequency as a function of the volume percent TBP ($0 \leq$ vol % TBP ≤ 35) in *n*-dodecane is linear. This result differs significantly from the second-order response expected for a simple binary mixture of TBP dissolved in *n*-dodecane and indicates that solute-solute interactions are significant. Petkovic[2] reported a value of 2.6 M^{-1} for the dimerization constant of TBP in *n*-dodecane. Including this chemical equilibrium into the response curve model satisfactorily explained the experimental results. Dielectric constant values of 3.09 and 8.23 were calculated for the monomeric and dimeric forms of TBP respectively. Average precision obtained with standard mixtures are <0.02% TBP; average errors are <0.1% TBP. Total time required to analyze a sample, including chemical pretreatment, is approximately 5 min. A manuscript summarizing this development effort has been submitted for publication.[3]

Work is in progress toward the development of a computer-controlled pipetter, which will replace present units designed during the early 1950s. The new pipetter incorporates a stepping motor drive for delivery of microliter aliquots and utilizes a linear variable displacement transducer for closed-loop control of the plunger position. The prototype pipetter will use the AIM 65 microcomputer as the controller. User operations are documented via an on-board printer. This instrument will significantly improve the solution handling operations within the hot-cell laboratories. *(L. N. Klatt, D. E. Goeringer)*

In-line sensor development for Consolidated Fuel Reprocessing Program. The Analytical Chemistry Division is continuing its joint effort with the Instrumentation and Controls Division (I&C) to develop chemical measurement systems for fuel recycle process control. Our primary responsibility is to develop measurement strategies for real-time analytical sensor systems where no commercial instrumentation is available. This past year, research and development has been completed on two new measurement techniques: one for the determination of uranium (20 to 200 g/liter) in either high or low acid and the other for the determination of free nitric acid (0.03 to 11 *M*) in the dissolver solution. New projects include the potential use of electrochemical methods to determine such parameters as the Pu(III)/Pu(IV) ratio or the presence of hydroxylamine or hydrazine in nitric acid process streams. This project is nearing completion. A second new project is the development of the algorithms that will permit the multiwavelength spectral determination of uranium and plutonium in organic streams. The continuing identification of high-priority sensor needs has necessitated an expansion of this effort in the next fiscal year.

Free-acid monitor. The project has been completed, and a report has been issued detailing its design and operation.[4] A patent disclosure has also been prepared, and application for a patent has been filed. A working prototype is currently under construction for installation in the fuel reprocessing demonstration plant.

Electrochemical in-line sensors. An investigation of the potential of in-line cyclic voltametry with solid electrodes is nearing completion. Vitreous carbon electrodes were found to be useful in the qualitative estimation of the Pu(III)/Pu(IV) ratio in the presence of uranium, hydroxylamine, hydrazine, and nitric acid. A semiquantitative (10%) estimate of the total plutonium (0.5 to 20 g/liter) in the process stream is also possible. Platinum electrodes can be used to qualitatively detect both hydroxylamine and hydrazine and may be used to monitor the oxidation of both compounds. A prototype monitor cell containing both platinum and vitreous carbon electrodes operated successfully for one month in a U, Pu, H_2NOH, N_2H_4, HNO_3 stream before precipitation of solution elements on the electrodes caused a loss of sensitivity. The sensitivity could be restored only by disassembly of the cell and by manually polishing the electrodes. This unpredictable loss of sensitivity is the major impediment to the application of cyclic voltametry to the in-line process analysis. A program is now in progress to develop a method of rejuvenating the electrode surface in situ. A report detailing this investigation is nearing completion and will be published as an ORNL/TM.

Uranium monitor. Aqueous streams in the fuel recycling process contain from 20 to 200 g of uranium per liter and up to 1 *M* free nitrate ion. These streams may either contain excess acid (0.5 to 4 *M* HNO_3) or be acid deficient (0.02 to 0.5 *M* HNO_3). The concentration of each stream component will vary by at least 10%. The visible spectra of uranyl solutions containing varying concentrations of acid and free nitrate ion were examined to develop a uranium monitor that could accurately operate under any of these variable stream conditions. The uranyl absorbance was found to be primarily the result of three uranyl species: UO_2^{2+}, $UO_2NO_3^+$, and a uranyl dimer of unknown composition. The concentration of HNO_3 in the stream determines the relative concentration of each of these uranyl species and, thus, their contribution to the total absorbance at a specified wavelength. Because UO_2^{2+} and $UO_2NO_3^+$ are the major uranyl species in streams containing excess acid, the absorbance at 416 and 426 nm can be used to simultaneously calculate the total uranium and nitrate concentration in a stream to within 5% and 0.5 *M* units respectively. The uranyl absorbance in acid-deficient streams is due primarily to the absorbance of UO_2^{2+} and the uranyl dimer. As a result, the absorbance at 416 and 426 nm can be used to simultaneously calculate the total uranium and hydrogen ion concentration in the stream to within 3% and 0.2 *M* units respectively. Once the operating range of HNO_3 concentration has been established for a given process stream, the appropriate simultaneous calibration equation can be applied to the 416 and 426 nm data. A derivation of the simultaneous equations has been published,[5] and an in-line monitor based on these equations is being fabricated by the I&C Division.

A similar study of uranyl absorbance is being undertaken for solutions of 30% TBP in *n*-dodecane. Preliminary results indicate that an analogous simultaneous calculation of total uranium and hydrogen ion concentration can be made for organic process streams. A description of the calibration equation will be published in the coming year.

The spectral characteristics of plutonium in aqueous solutions were also evaluated to determine if the uranium monitor could be modified to detect total plutonium, as well as to determine the Pu(III)/Pu(IV) ratio. Preliminary results suggest that 0.1 to 20 g of total plutonium per liter can be determined in the presence of uranium with an accuracy of approximately 5%. If the absorbance at 476 nm is monitored, 0.1 g Pu(IV) can be determined in a solution that contains predominantly Pu(III). Further spectral data are being obtained to determine the effect of other stream constituents on the plutonium analysis. *(D. A. Bostick, J. E. Strain, H. H. Ross)*

Spectroelectrochemistry in chloraluminate melts. Molten halides are of considerable interest in several areas of energy conversion and conservation, such as rechargeable batteries, fuel cells, and catalysis. Study of solution chemistry in molten-salt media is experimentally difficult and requires development of new analytical methodology. We are involved in the development of spectroelectrochemical techniques for investigations of molten-salt solutions. Spectroelectrochemistry involves the simultaneous acquisition of spectral and electrochemical data; the technique can be very useful in unraveling complex redox chemistry in solutions.[6]

The rapid-scan spectrometer system described previously[7] is being used for spectroelectrochemical studies of the oxidation and reduction mechanisms of several solute species in chloraluminate melts ($AlCl_3$-NaCl mixtures). Two types of optically transparent electrodes (OTE) are used in this research: platinum screens or thin slices of glassy carbon foam. In either case, light is transmitted through the electrode to record spectra of species generated at the electrode surface.

During the past year, we have emphasized the characterization of the positive oxidation states of sulfur in acidic ($AlCl_3 > 50$ mole %) chloraluminate melts. Although the electrochemistry[8,9] and spectroscopy[10] of this system have been studied independently, the use of spectroelectrochemical techniques has yielded much additional information on the mechanism of the oxidation of sulfur. Such information is valuable for the development of a sodium-sulfur(IV) molten-salt battery.[11]

The glassy carbon foam OTE was found to be especially useful because of its high surface area and the fact that optical pathlengths up to 2 mm could be obtained. This is important because most of the sulfur species have fairly small formal absorptivities (~100) in the visible and near infrared region. (Some problems were encountered, however, due to degradation of the carbon OTE in the melt for prolonged periods of time.) It has been suggested[12] that polarization of glassy carbon electrodes at positive potentials in chloride medium produces electrode instability, possibly due to the reaction of chlorine gas with the electrode. The extent of this problem in molten chloraluminate remains to be determined.

When sulfur is oxidized at a potential of 1.65 V vs Al(III)/Al reference electrode at a carbon OTE with temperatures in the range of 150 to 250°C, absorption maxima at 600, 730, and 980 nm are observed. Identical results are obtained with a platinum OTE. Based on published data,[10] the species responsible for these bands are most likely S_8^{2+} (600 nm) and S_{16}^{2+} or S_8^+ (730 and 980 nm). These species appear to exist in equilibrium at potentials between 1.4 and 1.7 V; however, the amount of S_8^{2+} increases as the potential is made more positive. A study of absorbance maxima vs potential for these absorption bands shows that the 730- and 980-nm bands reach a maximum absorbance at 1.60–1.65 V and decrease at higher potentials, whereas the 600-nm band achieves its maximum value at about 1.70 V. This fact reinforces the assignment of the 600-nm band to the higher oxidation state of sulfur.

A complementary electron spin resonance (ESR) study showed the presence of at least two paramagnetic species. The intensities of the ESR signals vs potential were very similar to the absorbance vs potential curves described above. It may be concluded that the two species giving rise to the 600-, 730-, and 980-nm absorption bands must be paramagnetic species (S_4^+ and S_8^+ respectively) or that these species are in equilibrium with their respective dimeric forms ($2S_4^+ \rightleftharpoons S_8^{2+}$ and $2S_8^+ \rightleftharpoons S_{16}^{2+}$). The fact that one ESR signal disappears at 250°C, while two species are still observed by absorption spectroscopy, supports the latter hypothesis.

Temperature dependence studies in the 150 to 250°C temperature range indicate that the lower oxidation state species become less stable relative to the higher oxidation state species with increasing temperature. At higher sulfur concentrations, the lower oxidation state species were found to be more stable relative to the higher oxidation state; however, the higher oxidation state always predominated at the higher potentials.

These results indicate that the oxidation mechanism of sulfur in this medium is very complicated, perhaps involving parallel oxidation pathways and coupled chemical equilibria. Work is continuing toward the development of a mechanism that will satisfactorily explain the experimental data. *(V. E. Norvell, G. Mamantov, L. N. Klatt)*

Analytical Spectroscopy

Laser spectroscopy studies. The study of resonance ionization spectroscopy (RIS) has continued[11] in cooperation with G. S. Hurst's group in the Health and Safety Research Division. Two invited review articles describing the general technique of RIS have been written this year.[14,15] In developing these reviews, five basic RIS schemes that could be used for most of the known elements, except He, F, Ne, and Ar, were devised and published. The inability to determine the four above-named elements is a laser energy limitation that will disappear as higher energy tunable lasers are developed.

The application of RIS to ultra-low-level (radioactive) counting applications in general, and ^{7}Be-acetylacetonate counting in particular, has continued. The requirement of time- and volume-element coincidence for a counting event, and the RIS detection of the expected daughter atom, reduces counting backgrounds by several orders of magnitude. This reduced background finds particularly useful application in future solar neutrino counting experiments that were mentioned last year[13] to be carried out with R. Davis of Brookhaven National Laboratory. Some problems have been encountered with the operation of a rather radical design heatable, position-sensitive, large laser (optical) volume-proportional counter that is to be used in this application. Most of these problems seem to be resolved now, and a prototype chamber is presently being tested for electron response prior to actual tests with ^{7}Be-acetylacetonate. The counter has a position sensitivity of about 1-mm FWHM over its effective length of 8 cm. Its operation at a temperature of 150°C is presently being evaluated. The effective optical volume, the active counting volume of the chamber swept by the laser, is 65% of the total chamber volume. In future chambers, this active volume will be increased.

With ^{7}Be, the recoil energy of the daughter ^{7}Li is 50 eV. There continues to be a question as to the charge state of this recoil species, or the lower initial energy recoil species, at thermalization. Perhaps the lower limit of a recoil species of this kind is the ion generated in the RIS process itself. If it is possible to neutralize this ion, it should be possible to cause the neutralization of any recoil ion. Further, if it is possible to quickly neutralize an ion created by RIS, one could have RIS with amplification (RISA) where an RIS active atom could be caused to emit 10 to perhaps 100 electrons during the period of a laser pulse. A discussion of this concept has been published,[16] and several schemes are being investigated to achieve the RISA effect. Presently being studied is a possible scheme that involves the formation of a weakly bound molecular species, $LiNO^+$, from Li^+ and NO, which might be dissociated to Li and NO^+ by interaction with an ultraviolet laser beam.

Two other areas of RIS applications are being pursued, primarily with conceptual studies and component development and fabrication. It should be possible to detect single plutonium atoms made from the α decay of ^{244}Cm in a chamber designed to stop the plutonium recoil atoms within a volume element to be swept by a laser beam. It is expected that plutonium can be detected by a two-photon, single-energy RIS scheme.[14,15] Components have been fabricated to investigate this application, but a chamber has not been assembled. In another area, very preliminary studies of the use of RIS as an element-specific ionization source for mass spectrometry have been pursued by personnel in the Mass Spectrometry section of the Analytical Chemistry Division. Components are presently being designed and fabricated to study the application of this technique to lanthanide samples in which several different lanthanides have identical masses but could be selectively photoionized by a two-photon, single-energy RIS scheme.[14,15]

In cooperation with C. E. Bemis, Jr., and J. R. Beene, Physics Division, the development of laser-induced nuclear polarization (LINUP)[16] has continued. The LINUP effect was demonstrated with ^{240m}Am, a spontaneously fissioning isomer of 0.001-s half-life. A paper describing this experiment has been written.[17] In this study the optical isomer shift in the $^8S_{7/2} \rightarrow {}^{10}P_{7/2}$ atomic transition in neutral americium has been measured for ^{240m}Am. Using a laser-excited optical pumping technique, this transition is found to be shifted by 0.26 ± 0.02 nm from 640.5 nm, the wavelength for this transition in normal americium. From a knowledge of the shift in this transition between ^{241}Am and ^{240m}Am and a knowledge of their nuclear radii, one can infer a difference in *nuclear mean-square radii* G(r^2) of 5.1 ± 0.2 fm^2 between the fission isomer and normal ground state americium. Considering reasonable model shapes for the americium nucleus, this difference in mean-square radii would imply an elliptical nucleus for the fission isomer whose major axis is twice that of the minor axis. These experiments provide the first direct experimental proof and measurement of the large deformations expected for the nucleus of a fission isomer. *(J. P. Young)*

Theoretical calculations in flame atomic absorption spectrometry. Flame Atomic Absorption Spectrometry (FAAS) is presently the most widely used technique for trace elemental analysis. This technique provides a sensitivity of less than 1 ppm for a large number of the elements with an instrument that is relatively inexpensive and simple to operate. Unfortunately, FAAS is not without its drawbacks. The measured response with this technique is quite dependent on the sample matrix composition. If this were not true, it would be possible to do absolute analysis with FAAS. Many researchers have tried to understand these matrix effects from a fundamental standpoint.[18] We have developed a new mathematical treatment of the FAAS process to examine experimental parameters that have not been considered previously. These new considerations involve the geometrical and spatial aspects of the Beer-Lambert law rather than the more usual spectroscopic parameters. The geometrical and spatial requirements of the Beer-Lambert law are (1) plane-parallel incident radiation, (2) an absorption cell of uniform cross section along the optical axis coordinate, and (3) a spatially uniform analyte concentration in the absorption cell. More precisely, the third condition can be relaxed to only requiring a constant number of analyte species in any volume element dxdy l, where l is the cell path length along the optical axis (also the z axis).

In this study, a typical FAAS optical system is assumed in which the source is imaged one-to-one at the center of a slot-type flame, and this image is again focused one-to-one on the entrance slits of a monochromator. The monochromator performs spatial selection at the source and thus specifies the optical path through the absorption cell (flame).

The absorption cell is assumed to be of rectangular cross section in the x-z plane, where the z axis is along the optical axis, the y vector is parallel with the monochromator slit height, and the x axis is orthogonal to the other two. The cell will have infinite extent along the y axis, and the rectangular x-z cross section is of uniform width and length. The optical beam profile accepted by the monochromator, which traverses the absorption cell, can be suitably described with geometrical optics. Two different optical beam profiles are modeled. In one case, a very small slit height is assumed. This slit height would result in a beam profile in the absorption cell whose surface would be that of two opposed cylindrical cones, with their apexes meeting at the center of the cell. In the second case, the slit height is much larger than the slit width. This latter situation results in an opposed wedge-type beam profile passing through the cell. In both cases, the apex angle of the beam profile is equal to the acceptance angle of the monochromator. For a typical FAAS experiment, an $f/8$ monochromator would be utilized; this would correspond to an acceptance angle of 7°. Such an f-number is assumed in this work.

Obviously, this optical system–atom cell combination does not comply with the first Beer-Lambert law requirement stated previously. First, a ray normal to the absorption cell has a path length that is different from that of a skew ray. This is of little consequence for the weak $f/8$ optical system and results in only 0.06% error in an absorption measurement. It is significant, however, that the absorption cell width in FAAS would typically be less than the greatest width of the beam profile. Effective absorption cell widths in FAAS have been found to be in the range of 2 to 4 mm.[19] The width of the above-described beam profiles for a 10-cm-cell length would be 6 mm. Significantly, the shortest path length could be only 60% of that for normal incidence.

Calculations were performed to yield the absorbance for the models; a uniform analyte concentration was assumed. For a 2-mm-cell width, the absorbance was 27% and 18% lower than that predicted by the Beer-Lambert law for the wedge- and cone-shaped beams respectively. The above-stated errors are for an expected absorbance of 1.0. These errors essentially diminish to zero as the cell width approaches 6 mm. The resultant working curves are also nonlinear but not significantly in the 0–1.0 absorbance range.

The third requirement of the Beer-Lambert law, stated earlier, is also not met in FAAS. The atom density in the flame is a smoothly varying function of both the x and y coordinates (i.e., across the width and height of the flame). Because the atom density changes relatively slowly with height, only a concentration profile as a function of width is used in our model. A parabolic atom density profile, when substituted into the above model, further reduces the sensitivity of the FAAS measurement. At an absorbance of 1.0 and a cell width of 2 mm (distance between zeros of parabolic profile), the relative error is 47% for the wedge-shaped beam.

These results show that geometrical and spatial aspects of the FAAS experiment would be important design parameters if an absolute analysis method were to be employed. In addition, the effect of the cell width on the measured absorbance could limit the precision and accuracy of a determination using the standard, relative analysis method. The loss of precision and accuracy would arise because the width of the atom density profile is dependent on sample matrix. It may be possible to circumvent these experimental problems by designing a burner that more closely matches the optical beam profile.

The mathematical framework of the above model suggests the possibility of errors arising due to temporal fluctuations in the analyte concentration. Such fluctuations are well known as analyte flicker noise in FAAS. If the detection system integrates over these fluctuations, the results will be in error; that is, the average absorbance signal does not equal the absorbance of the average analyte concentration. This effect is shown to introduce only very small errors for reasonable absorbance and noise levels. *(J. M. Ramsey)*

Photoacoustic spectroscopy. Pulsed laser-excited photoacoustic (PA) spectroscopy can be valuable for the analysis of solids and powders, especially for materials that exhibit sharp absorption spectra.[20] Our study of this technique was concentrated in two major areas this year: (1) instrument calibration and characterization and (2) signal generation mechanisms. In addition, an inexpensive pulsed laser power meter based on our Helmholtz resonator (HR) cell[21] has been developed and tested.

At the time of our last report, only relative intensity information could be obtained with our laser PA spectrometer. Absolute data are of course desirable, especially for cell calibration factors, cell background levels, ultimate detection limits, and signal linearity with input laser power and sample absorptivity. With the acquisition of a commercial laser power meter (thermopile), it became possible to calibrate both our open-cavity[20] and HR cells in terms of PA signal strength for a given input optical energy. Data were taken for black felt (a near "perfect" absorber), silica gel (a scattering but nominally nonabsorbing powder), the empty HR cell, and a set of holmium oxide powder samples "diluted" with silica gel. For black felt, the calibration factors (CF) for the open-cavity cell were found to be 3.8 mV/mJ and 16 mV(p-p)mJ for the low- and high-frequency signal components respectively. The calibration factor for the HR resonator cell is 39 mV/mJ for black felt. As expected, based on the ratio of cell interior volumes, an acoustic gain of ten is thus obtained with the HR cell relative to the open-cavity cell. The background signal for the empty HR cell is less than 1% of the signal for black felt, a sixfold reduction from the open-cavity cell. Excellent signal linearity was observed as a function of input laser energy over a wide range (*vide infra*). The linearity of the PA signal strength was determined with regard to sample absorptivity. A set of powder samples of varying weight fraction was prepared by "diluting" holmium oxide powder with silica gel. The working curve for

PA signal strength at the wavelength of maximum absorption was found to be linear with the Ho_2O_3 weight fraction. This finding is in contrast to reflection spectroscopy data taken for the same set of samples. In the latter case, the measured reflectivity is highly nonlinear with weight fraction; a linear working curve can, however, be obtained if the Kubelka-Munk theory is used to modify the raw reflectivity data. By extrapolating the holmium oxide PA working curve to a low weight fraction and assuming that the cell background can be subtracted exactly, the overall system electronic noise sets a detection limit (signal to noise ratio = 3) of 78 μg of holmium oxide for a 30-mg sample. However, the errors introduced by wavelength repeatability and cell loading (repeated analyses of the same sample) result in a ±5% uncertainty for any individual analysis. For a more homogeneous sample, the latter may be reduced significantly.

For open-cavity cells, the PA signal waveform is highly dependent on both cell geometry and sample. For example, the high- to low-frequency signal component ratio varies widely.[20] This waveform variability might be explained if one or more of several signal generation mechanisms are operative in addition to the accepted PA phenomenon.[22] These possibilities include particle size effects, adsorbed gas effects, and thermally derived surface distortions. Various studies were undertaken to evaluate these possibilities.

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By examining the PA waveform for various open-cavity cells, it has been determined that the dominant component of the high-frequency PA signal is actually due to excitation of a resonance of the microphone in the enclosed cell configuration. If this signal had been due to standing acoustic waves in the cell cavity, the resulting resonant frequency would have changed with changes of the cell dimensions. The high-frequency signal component scales approximately as $1/R$ (where R is the sample-microphone separation), while the low-frequency, damped oscillation scales as $1/V$ (where V is the cell volume).

The HR PA cell acoustically stretches short optical pulses into the millisecond time regime and, as such, can be utilized as the detector for a simple and inexpensive pulsed laser power meter. Such a device has been breadboarded and tested. Black felt is used as the target in the HR cell. The microphone signal is offset (to eliminate the microphone bias voltage) and amplified in a two-stage operational amplifier preamplifier (gain = 50). The preamplifier output is sampled by a sample-and-hold (S/H) amplifier that is triggered by the trailing edge of a monostable multivibrator pulse. The pulse duration is determined by adjustable RC circuitry so that the trailing edge is positioned in time at the peak of the amplified acoustic pulse. The one-shot is itself triggered in any of three ways: (1) by an electrical synchronization pulse from the laser, (2) by the output of a photodiode/comparator combination, or (3) manually.

Because the microphone pulses peak at approximately 1 ms, the S/H amplifier can be configured with adequate speed to accurately acquire the pulses, yet still "hold" them with minimal droop between pulses. To remove reset spikes and to reduce some of the pulse-to-pulse laser noise, the S/H amplifier output is smoothed by a low-pass filter with a 1-s time constant.

The linearity of this simple power meter (see Fig. 1.1) was determined over a 3.5-decade range (0.58 μJ to 2.9 mJ per pulse). Comparison data were

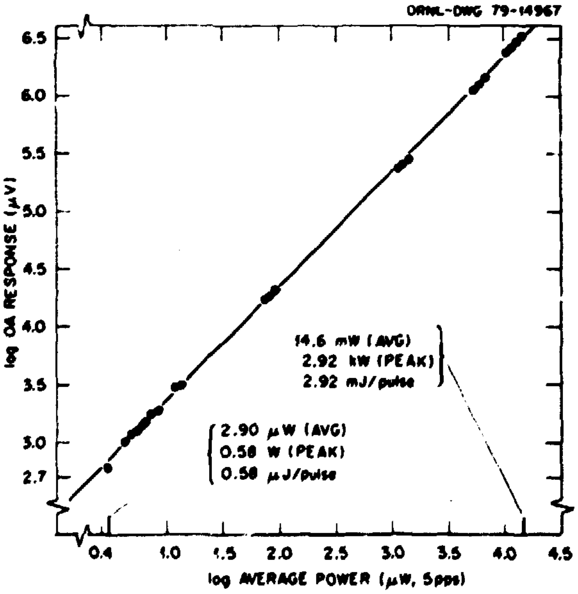

Fig. 1.1. Photoacoustic (PA) laser power meter linearity.

taken simultaneously with the PA power meter and a gated-integrator photometer that had been standardized with a thermopile detector. The linear regression correlation coefficient for these comparison data was 0.9999. The lower power extreme of the plot indicates the sensitivity limit of the PA power meter; the other linearity range extreme is limited by the maximum output power available from our laser. The ultimate upper limit is set by the cell target material that will withstand up to approximately 50 mW average power. The response has been satisfactorily tested for input optical pulses from 1 ms to 10 ns.

The PA power meter is distinguished from other pulsed laser power meters by several definite advantages. Thermopile detectors are slow and are subject to thermal drift. Photodiodide-based power meters saturate at the high peak powers of pulsed lasers, require complex electronics for fast pulse detection, and do not exhibit a flat spectral response. The PA power meter circumvents all of these problems. In addition, the simplicity of the PA power meter allows for inexpensive implementation (about $200). *(R. W. Shaw)*

Applications of fiber optics in optical spectroscopy. The continuing improvement in the ability of fiber optic waveguides to transmit light over long distances has made practical several unconventional applications in analytical instrumentation. The transit time of a light pulse through a fiber and its variation with wavelength can be used to obtain spectral dispersion in the time domain. Multiwavelength spectroscopy can be performed with a single detector, a mechanically rigid system, and inherent nanosecond time resolution. We have under development two types of fiber optic spectrometers. The first uses the wavelength dispersion of the fiber for time-of-flight separation of the spectral components. The second uses an array of fibers of different lengths to bring sequentially to a single detector the spatially dispersed output of a grating spectrometer.

Because of the attenuation of the fibers, their lengths should be as short as permitted by the time resolution of the system. A single-photon counting technique, often used to measure short fluorescence lifetimes, has been used to obtain nanosecond time response for the two spectrometer systems. In this method, light from a pulsed source of broad spectral bandwidth is attenuated until, at most, one photon per flash is detected. The arrival times of the detected photons, which can be determined with subnanosecond precision, are a function of their wavelength because of the dispersion of the instrument. The desired spectral information is obtained from the distribution of photons counted vs arrival time after a large number of counts has been accumulated. Among the advantages of the single-photon counting technique are the low source intensity required, the use of readily available modular electronics, and convenient digital output for subsequent calculations.

A dual-beam time-of-flight spectrometer has been developed that is based on the variation of transit time with wavelength.[23] Two optical fibers are used, with lengths of 525 and 550 m. Light pulses from the source are divided by a beam splitter so that they pass through a sample cell into one fiber, or through a reference cell into the other. Both fibers are butted against the photomultiplier. Because one fiber is longer than the other, the sample and reference spectra have different time delays and can be measured concurrently. This instrument has been described in a recent article.[24]

The second type of spectrometer under development uses a number of fibers of different lengths to time-delay multiplex a set of simultaneous pulses of different wavelengths onto a single photomultiplier. A pulsed source is spatially dispersed by a grating monochromator with the exit slit removed. Approximately monochromatic pulses of the dispersed light are collected by an array of individual fibers located at the exit plane of the monochromator, delayed by the transit time of the various fibers, and detected sequentially by the photomultiplier. The incremental time delay of the fibers is chosen to be greater than the time resolution of the instrumentation. The spectral resolution that can be attained is therefore governed by the dispersing monochromator and fiber placement rather than by fiber length or instrumental time resolution.

The initial version of this time delay multiplexing spectrometer uses an array of 30 fibers with lengths ranging from 1 to 59 m. The 2-m increment gives a delay of approximately 10 ns between successive fiber channels, well above the 2-ns time response of the instrumentation. The input light pulses are dispersed by a 600-groove-per-millimeter grating in a 20-cm focal length monochromator. Spectral resolution in this configuration is 3 nm per channel. The 90-nm coverage can be chosen anywhere within the 250- to 900-nm range of the instrument. *(W. B. Whitten)*

Determination of inorganic fluoride. To detect traces of fluorides in natural waters and residues, an inorganic or organic fluorine compound is volatilized into a stream of helium that passes through a glow discharge, and the intensity of the fluoride emission line is measured. Volatile inorganic fluorides (HF, BF_3, SiF_4) can be produced by heating the reactants in a small platinum furnace located a short distance upstream from the discharge. In preliminary experiments, 20 ng of fluoride, volatilized in this way, produced a peak that lasted 70 s. Efforts are now directed toward making this peak narrower and taller and toward applying the technique to solids.

Certain volatile organic silyl compounds have been shown[25] to react with aqueous dissolved or suspended fluorides, forming an extractable silyl fluoride. It was hoped that this type of extract could be analyzed directly by the glow-discharge technique. First, however, it was necessary to show that the mixture in question would not introduce spectral or other complications into the procedure. Preliminary experiments showed that organic molecules can interfere in two ways with the generation of fluoride spectral emission lines: (1) by reducing the efficiency of excitation and (2) by producing molecular emission bands that overlap the fluoride line, generating a false signal. The quenching effect can be minimized by using an extractant in which the silyl compound is less volatile than the solvent. The spectral overlap effect can be overcome by using a background corrector capable of disregarding any molecular band emission that may accompany the transient fluoride signal. To do this, an oscillating refractor plate (ORP)[26,27,28] system was assembled and modified to use with a Jarrell-Ash 0.5-m Ebert monochromator. With the ORP in place, a weak fluoride signal gave the same response in the presence or absence of a noisy background continuum 130 times as intense as the fluoride line.

The two extractants that looked most attractive for this type of technique were solutions of triethylchlorosilane and diphenyldichlorosilane dissolved in di-isopropyl ether (DIPE). These chlorosilanes, after contacting the aqueous fluoride solutions, would exist in the extract as the corresponding fluorosilanes. Relative volatility testing was therefore performed on solutions of triethylfluorosilane (TEFS) and diphenyldifluorosilane (O_2SiF_2) in DIPE. In these tests, the ORP was used to discriminate between signals at 685.602 nm due to fluoride and those due to C_2 bands. The tests showed that the volatilization curves of TEFS (bp 110°) and DIPE (bp 62°) overlap considerably in time, despite the difference in boiling points. However, DIPE was easily eliminated from a DIPE-O_2SiF_2 mixture without loss of O_2SiF_2 (bp 157° at 6.66 kPa). After evaporation of the solvent, the residue of O_2SiF_2 might thus be vaporized into the discharge from either the plutonium furnace or the cathode surface.

The most detailed study so far has been made by evaporating 1 μl of O_2SiF_2-DIPE solution on the surface of the cathode, waiting a few seconds for the DIPE to evaporate, and volatilizing the residue in a 50–100-mA glow discharge. Cathodes of many sizes, shapes, and materials have been tested; the best procedure so far appears to be to evaporate the residue on the end face of a 1.52-mm-diam tungsten (2% ThO_2) welding rod. With this technique, using the background corrector, the present limit of detection is 1×10^{-10} g ($RSD = 10\%$). These results will now be compared with those obtainable by evaporating the same residue with the plutonium furnace. *(C. Feldman)*

Time-resolved laser spectroscopy. A new project is being initiated in laser applications to analytical measurements. Initially, time-resolved spectroscopic measurements are to be employed to determine their usefulness in analytical measurements. Up to now, temporal resolution has been little used because of the difficulty and expense in making such measurements within the brief time scale required. Lasers, when coupled with new inexpensive detection systems, can provide the needed temporal resolution.[29]

Equipment has now been procured for this project. Initial experiments are to be performed with a newly acquired mode-locked argon-ion laser that can be tuned to emit radiation at any of 11 essentially discrete wavelengths in the ultraviolet and visible parts of the spectrum. Continuous wave radiant powers obtained at these individual lines range from a few hundred milliwatts to several watts. The argon-ion laser can be actively mode locked at most of its lasing wavelengths. When operated under the mode-locked condition, the laser emits a train of optical pulses with durations of ≅100 *ps* and a repetition rate of ≅100 MHz. The peak powers when mode locked can be as large as 100 W for this specific laser. Because of the spatial coherence of this laser, peak irradiances of ≅250 $\mathrm{MW \cdot cm^{-2}}$ are obtainable. Obviously this laser has many desirable characteristics for use in time-resolved spectroscopic experiments.

In addition to the laser, optical components and electronic detection equipment have been purchased and constructed. An important optical component is the aluminum honeycomb optical table that allows one to construct and modify optical measurement systems with ease. A high-speed photodiode ($T_r < 50$

ps) a necessary diagnostic tool when using mode-locked lasers, was constructed. A high-voltage Schottky switching diode was mounted in a 50-Ω holder similar to a previous design,[30] to achieve the rapid response. *(J. M. Ramsey)*

Spectrophotometric studies at the Transuranium Research Laboratory. In cooperation with J. R. Peterson of the University of Tennessee and R. G. Haire, Chemistry Division, and various visitors to the Transuranium Research Laboratory (TRL), we continued spectrophotometric studies of transuranium and related compounds.[31] Our involvement is mainly with the application of spectral techniques to the identification and characterization of such compounds as they are related to the interests of the heavy element research program of the Office of Basic Energy Science. We have developed[32] a microscope-spectrophotometer capability that can effectively characterize solid state samples, or sample areas, as small as 5 μm^2; spectral examination becomes an extremely sensitive tool to determine, for example, ion identity, oxidation state, or coordination.

The progeny growth studies described last year[31] continue, and the conclusions drawn from last year's initial results have not been altered in following α and β decay of halides. It still seems apparent that oxidation state and crystal structure are preserved in β decay, and there is some evidence that they are preserved in α decay. These studies are being expanded to other anions, and preliminary data suggest that the oxidation state may not be preserved in α decay of oxyanion compounds, perhaps including oxides but not including oxyhalides. Some of the work with oxyanions (phosphates) is just getting under way; the results with oxides are the outgrowth of work that included J. Y. Bourges, a visitor from the French Atomic Energy Commission. In a final experiment with the new orthorhombic form of $CfBr_3$ that resulted from the β^- decay of orthorhombic $^{249}BkBr_3$(6), the $CfBr_3$ was slowly heated while following the absorbance of a peak known to be associated with this crystallographic form of $CfBr_3$. At 360°C, the peak rapidly disappeared, and the $CfBr_3$ was transformed into normal monoclinic $CfBr_3$. A paper describing this study, which has followed the ingrowth of californium into $^{249}BkBr_3$ over more than a 3.5-year period (close to four half-lives of ^{249}Bk) has been written.

Two other areas of the study of progeny growth in halides received some attention. We have attempted to produce $BkBr_2$ by the reduction of $BkBr_3$ with H_2 or with berkelium metal. In both cases no reduction of Bk(III) was observed spectrally, but it was quite apparent that the californium daughter was reduced to Cf(II). The mechanism of how a Cf(II) granddaughter is generated from ^{253}Es(II) compounds remains a mystery. The other area of study involves trying to establish material balances of progeny species. It seems apparent in β decay studies of californium that all BkX_3 can be accounted for as transmuting to CfX_3. The ability to assess quantitative information from spectra derived from a single-beam spectrophotometer is limited, but work this year suggests that, at least in the tribromide case, we can only account for half of $^{253}EsBr_3$ parent as transmuting to $BkBr_3$. It must be assumed that the rest of the berkelium daughter has no recognized local order that would be required for spectral identification. In an attempt to resolve this matter, we have compared aged ^{253}Es compounds derived from several different sources, namely, 86-day-old $EsBr_3$ and a tribromide product made from 86-day-old Es_2O_3. At 86 days, the berkelium daughter concentration from decay will be a maximum of about 85% of the sample. In a recent study, it was found that similar $PuBr_3$ concentrations were observed in a five-year-old sample of $^{244}CmBr_3$ ($t_{1/2}$ = 18 years) and in a tribromide sample made with five-year-old curium metal.

In connection with the work done with J. Y. Bourges, we were successful in obtaining some of our first spectra of oxides, and we used the spectral technique to follow the extent of oxidation of pure trivalent transuranic oxides or these oxides mixed with cesium or barium oxides. The results of this project are still being assessed, but it is known that Es_2O_3 could not be oxidized under any of our experimental conditions, while plutonium, americium, and curium oxides in proper mixtures with cesium or barium were oxidized beyond the (IV) state. Berkelium(IV) in a BaO matrix was spectrally identified; this oxidation state would be expected for berkelium.

The study of possible dimorphism in certain light actinide and lanthanide halides described last year[31] has continued. Spectral characterization was used to identify and follow the synthesis and transformation of several lanthanide and actinide triiodides. A paper has been written describing the work on NdI_3, SmI_3, and NdOI.[33] In that paper, a new hexagonal form (BiI_3 type) NdI_3 is characterized by x-ray powder diffraction and absorption spectrophotometry. With AmI_3, a new orthorhombic form ($PuBr_3$ type) has also been characterized by both x-ray and spectral techniques. Thus, although it was formerly thought that NdI_3 and AmI_3 were among the transition types between orthorhombic and hexagonal crystal structures of the rare earth triiodides, this is not the case. These triiodides can be prepared and transformed into either structure. *(J. P. Young)*

PHYSICOCHEMICAL ANALYSIS

L. D. Hulett, Group Leader

Electron Spectroscopy Studies

Electron spectroscopy. We have entered into a cooperative effort with the Instrumentation and Controls Division to investigate nickel cathode surfaces for the ORELA electron gun. Past methods of cleaning and preparing these surfaces have led to unpredictable results. The criteria for determining the quality of the cathode involves installation and testing through normal operation of the accelerator. A faulty cathode, therefore, results in a costly loss of time and funds. This problem has also been encountered at other installations. We are using x-ray photoelectron spectroscopy (XPS) to study the surfaces of the cathode at successive stages of preparation. Our initial results have shown that detrimental deposits are introduced by two of the aqueous cleaning procedures and that a hydrogen firing operation deposited silicon and titanium. Spectra of an electropolished 5% Zr, 95% Ni cathode alloy showed an enrichment of zirconium at the surface, a desirable condition for these surfaces. However, the elements from the electropolishing media were being incorporated in the surface. We are working toward establishing procedures for obtaining clean surfaces. These surfaces will then be corrected to cathode performance in the electron gun facility.

In another study, XPS is being used to investigate titanium corrosion. This is a cooperative study with A. L. Bacarella (Chemistry Division), who is studying the mechanisms of titanium metal corrosion in aqueous systems by electrochemical methods. He observes from current vs controlled potential measurements that the application of increasingly anodic potentials causes the oxidation current to increase to a maximum value and then decrease as passivation occurs. Knowledge about surface layers in the passivation region is of general interest in corrosion science as it relates to the problem of preventing destructive transformation at metal surfaces. The first objective in this study is to determine if a correlation can be made between titanium electrode potentials and bulk oxide formation on the surface. The XPS spectra of electrodes oxidized in sulfuric acid solutions containing chromium(II) show incorporation of chromium and sulfur in the titanium oxide film. The presence of sulfur appears to be directly related to the presence of chromium. Similar experiments performed in sulfuric acid, in the absence of chromium, showed no evidence of sulfur in the titanium oxide layers. The amount of sulfur and chromium present appears to be related to the passivation potential. This relation would be expected if the oxide layer thickness were also a function of the passivation potential. Variations have also been noted in the oxygen 1*s* photoelectron peak. This variation is not completely understood and will be studied further.

Investigation continued to determine whether concentrations of certain metal ions in natural waters may be controlled by oxidative sorption processes on manganese dioxide surfaces.[34] The determination of chemical shifts in photoelectron binding energies for this work required a precision in measurement that was, heretofore, not attained with our instrumentation. As a result, a new approach was developed that provides a standard deviation of 0.05 eV or less for the precision of repeated determinations of kinetic energies of photoelectron peak position. It has also become evident that some development will be necessary to produce standard reference materials for the continuation of this work.

Precise methods for calibrating the magnetic and electrostatic photoelectron spectrometers have been developed. Calibration data show that the spectrometer factors for both instruments are linear within ±0.01% for kinetic energies up to 1500 eV. There are apparent baseline shifts, however, which make frequent calibrations necessary. This characteristic of both instruments requires further evaluation.

A new sample chamber for the magnetic instrument has been designed and constructed using a rack and pinion sample transport system. The new design eliminates several lubricated surfaces, which have been a source of contamination, and provides improved seals with metal-sealed flanges. Eight samples, approximately 0.5 by 2.0 cm, can be loaded at one time, or larger samples can be used by changing the sample head. This sample handling system is also compatible with a drybox, which has been renovated for sample preparation and subsequent analyses without intervening exposure to the atmosphere. The drybox has moisture and oxygen traps, as well as monitors and facilities for evaporating materials onto surfaces for preparing standards.

An electrostatic electron spectrometer, which can be externally aligned within the stage chamber of the AMR-900 scanning electron microscope (SEM), was designed and constructed. The simplicity of the spectrometer, originally designed by Allen,[35] made it readily adaptable to miniaturization for use in the SEM. The system will be used for analyzing very small particles by x-ray photoelectron spectroscopy (XPS) and by photoelectron analysis of x rays (PAX), a method originally developed by Krause[36] for measuring low-energy x rays with high precision. In the XPS mode, the SEM electron beam will be used to generate K_α x rays from an aluminum foil very near the sample.

The Auger- and photoelectrons excited from the sample by these x rays will be energy analyzed by the spectrometer and detected with a channeltron electron multiplier. In the PAX mode, the SEM electron beam will be used to generate multiwavelength x rays from the sample. These x rays, in turn, excite photoelectrons from the aluminum foil. Energy analysis of these photoelectrons allows the identification of the x rays coming from the sample. (*J. M. Dale, H. W. Dunn, L. D. Hulett, E. Ricci*)

Transmission and scanning electron microscopy. The Chemical Technology Division—with G. Strandberg, principal investigator—is studying the feasibility of using microorganisms to decontaminate nuclear waste. A strain of *Pseudomonas aeruginosa* was added to a solution containing 100 ppm uranium. Wet chemical analysis showed that the bacteria absorbed the uranium to the extent of 4% by weight. Transmission electron microscopy was then used to study how the uranium was incorporated within individual cells. Many, but not all, were found to have needle-like inclusions on their walls and interiors. The microscope used in this study was equipped with an energy dispersive XRF spectrometer. By recording the XRF spectrum excited by the electron beam striking the inclusions, the presence of uranium was confirmed. A transmission electron photomicrograph of *Pseudomonas aeruginosa* containing uranium inclusions is shown in Fig. 1.2.

Physical and chemical methods of separating coal, such as magnetic extraction and plasma etching, are being evaluated by staff members of the Chemistry Division. We used scanning electron microscopy to examine magnetically separated specimens prepared by E. L. Fuller. For both magnetic and nonmagnetic fractions, layered structures were found. Crystallites of $CaCO_3$ and sand were imbedded in surfaces. Particles containing Si, Al, Ca, Fe, and possibly clays, were observed. In one of the unseparated samples from Kentucky, a particle of pure FeS_2 was found. The major heavy elements were S, Al, Si, Ca, Fe, Cu, P, and K for both eastern and western coals. Iron was present in both magnetic and nonmagnetic fractions. R. A. Strehlow has successfully used plasma oxidation to determine the inner structure of coal. The organic material was removed by bombardment with an oxygen plasma, revealing occluded inorganic materials arranged in undisturbed configurations. The morphologies of montmorillonites and kaolinites were studied. Submicron clay flocculates interlayered between coal particles were found, making possible a better estimate of how clays affect coal-burning kinetics.

Problem solving, using electron microscopy, is a major activity that involves a coordinated approach with the group in which the problem evolved. A recent example was the identification of corrosion scale on a stainless steel surface in a liquid potassium heat exchanger. Corrosion films were stripped from the boiler surface and examined by scanning electron microscopy with its associated energy dispersive x-ray fluorescence (SEM-EDX) to determine morphology and elemental composition. These data were combined with XRD measurements of crystal structure. Using these combined techniques, the corrosion products were identified as $FeCr_2O_4$ and αFe_2O_3. Another problem involved a study of filters made by polymerizing polyurethane in such a manner that structures of packed microspheres with open pores between are produced. Scanning electron microscopy was used to measure sphere shape and pore size as a function of polymerization temperature and time. Better porosity conditions resulted from polymerizing the filters at 0° C, which required curing times of 24 h.

Fundamental studies of molten-salt processes related to battery and fuel-cell design are being done by C. E. Vallet of the Chemistry Division. This project is being coordinated so that the researcher performs hands-on measurements with the microscope. Cylindrical frits, made of silica, are impregnated with fused mixtures of $AgNO_3$ and $NaNO_3$. Electrodes are placed at the ends of the cylinders, and the mixtures are electrolyzed at varying levels of current and temperature. The electrolysis causes diffusion gradients in the concentration of sodium and silver at the surfaces of the two electrodes. After sufficient times for steady states to develop, the salt mixture is quenched rapidly, while still undergoing electrolysis, in an attempt to freeze the concentration gradients in place. The cylinders are then dissected axially, perpendicular to the electrode surfaces, and

ORNL-PHOTO 1242-80

Fig. 1.2. Uranium inclusions in *Pseudomonas aeruginosa*.

the salt-electrode interfaces are analyzed by the SEM-EDX method. Results show that the Ag^+ ion is depleted at the cathode and enriched at the anode, in agreement with predictions made from considerations of ionic mobilities. (*F. L. Ball, R. L. Sherman*)

X-ray Methods

X-ray diffraction. The most widely used method available for inorganic compound identification is probably XRD. A very common procedure used by our group and many others is to combine XRD for crystal structure determination with XRF for elemental analysis. For example, in the previous section on electron microscopy, the identification of $FeCr_2O_4$ in a corrosion scale was mentioned. This was done by first examining the individual particles by SEM-EDX to determine if iron and chromium were present. Next the particles were examined in the Debye-Scherrer camera and found to have a spinel-type crystal structure. Because $FeCr_2O_4$ is known to be a spinel, we have a confirmed identification. Many such analyses are done on a routine basis. Probably the most interesting nonroutine work with the Debye-Scherrer camera this past year was done in conjunction with C. E. Bamberger and P. R. Robinson of the Chemistry Division, who are studying chemistries of hydrogen-oxygen cycles used in energy production. One of their processes involved the following reaction for oxygen generation:

$$2CeO_2 + 3Na_4P_2O_7 \rightarrow 2Na_3Ce(PO_4)_2 + 2Na_3PO_4 + {}^1\!/_2O_2 .$$

The existence of the Na-Ce double phosphate had never been established, and its diffraction pattern was not in the ASTM files. The double phosphate was successfully synthesized by another reaction mechanism:

$$CePO_4 + Na_3PO_4 \xrightarrow{\text{fusion}} Na_3Ce(PO_4)_2 .$$

The diffraction patterns of the double phosphates produced by the two different reactions were identical. This work has been submitted for publication.

Quantitative analysis by XRD using a modified XRD-5 (GE trademark) diffractometer has now become routine. In the 1978 Analytical Chemistry Division Annual Report, the addition of a post monochromater to our older model XRD-5 was described. This greatly improved sensitivities by reducing background from fluorescence and scattered radiation. Electronic improvements have reduced backgrounds even more. To correct for sample inhomogeneities, which cause preferred orientations of certain types of crystals, a sample rotator was installed. During this past year, the upgraded XRD-5 has been used extensively for quantitative analysis of asbestos in building materials. Aspirin (sodium acetylsalicyclic acid) has a *d*-spacing close to that of asbestos. It is ground into the sample as an internal standard. Detection sensitivity is about 0.1% for chrysotile asbestos

In testing building materials, such as ceiling tile, for asbestos, we often encounter gypsum as a common interference. We found that this could easily be eliminated by heating the sample to 300°C, dehydrating the gypsum, and changing its crystal structure so that it no longer had a *d*-spacing the same as asbestos. Care must be taken not to heat the specimen above 300°C, however, or the asbestos crystals will also be altered. The Occupational Safety and Health Act requires that asbestos concentrations in building materials be below 1% by weight. The optical microscope and the x-ray diffraction procedure using the XRD-5 were used as an initial test. For particles larger than 1 μm, birefringence and refractive index measurements were made. If the diffraction peak intensity indicated a concentration greater than 1% and the optical microscope did not detect asbestos, the sample was studied by transmission electron microscopy to determine if asbestos was present as submicron particles. Asbestos assay is one of the more tedious and difficult analytical procedures. This past year about 40 specimens of building materials were processed.

Crystallite size in solid materials is often of interest. If the crystallites are sufficiently small, less than 2000 Å, their sizes can be determined from the breadth of their diffraction peaks. It can be shown that diffraction peak width is inversely proportional to crystallite size. A large number of analyses have been done this past year on zirconium organophosphate compounds used in chromatographic processes and on uranium oxides in sol gels. (*R. L. Sherman, H. W. Dunn*)

X-ray Fluorescence. Recent additions to the XRF system in Building 4500N have increased its efficiency as a research and development and a service tool. X-ray excitation may be done by a silver-anode tube or by ^{241}Am or ^{55}Fe isotopic sources. These interchangeable sources make it possible to excite the K_α lines of all elements between sodium and thulium, which is of distinct advantage for generating easily interpretable spectra. With the silver source, it is possible to excite the *L*-spectra of all elements, both heavy and light. For doing fundamental parameter (absolute) quantitative analyses, the silver tube output is filtered to allow only AgK$_\alpha$ radiation to strike the specimen, thus precisely defining the cross sections for excitation. In past reports, we have described the use of fundamental parameter matrix corrections for processing XRF data from stainless steels and other materials. For other applications, however, such as the zirconium/hafnium program (described below), it has been found advantageous to filter the silver radiation with nickel foils so that the sample is excited mostly by bremstrahlung. The use of filtered radiation reduces the Compton scattered background. The system also has a versatile specimen mount that accommodates large and irregularly shaped objects and solutions.

A 90-position automatic sample changer is the most important accessory added this past year. It has allowed unattended overnight operation, which greatly improves work efficiency. Figure 1.3 shows a general view of the changer and Si(Li) detector mounted on a goniometer. Samples are placed inside or on the faces of small bakelite cups, which are then positioned in the three-tiered array of holes on the periphery of the rotating/translating drum. A PDP-11/04 computer steps each of the specimens into position for analysis. The spectrum, after being recorded by the Si(Li) detector, is deconvoluted by the computer, and the data are quantitatively processed and printed out by a matrix correction program. A unique feature of this sample changer design is the ability to determine sample inhomogeneities; that is the changer can be programmed to

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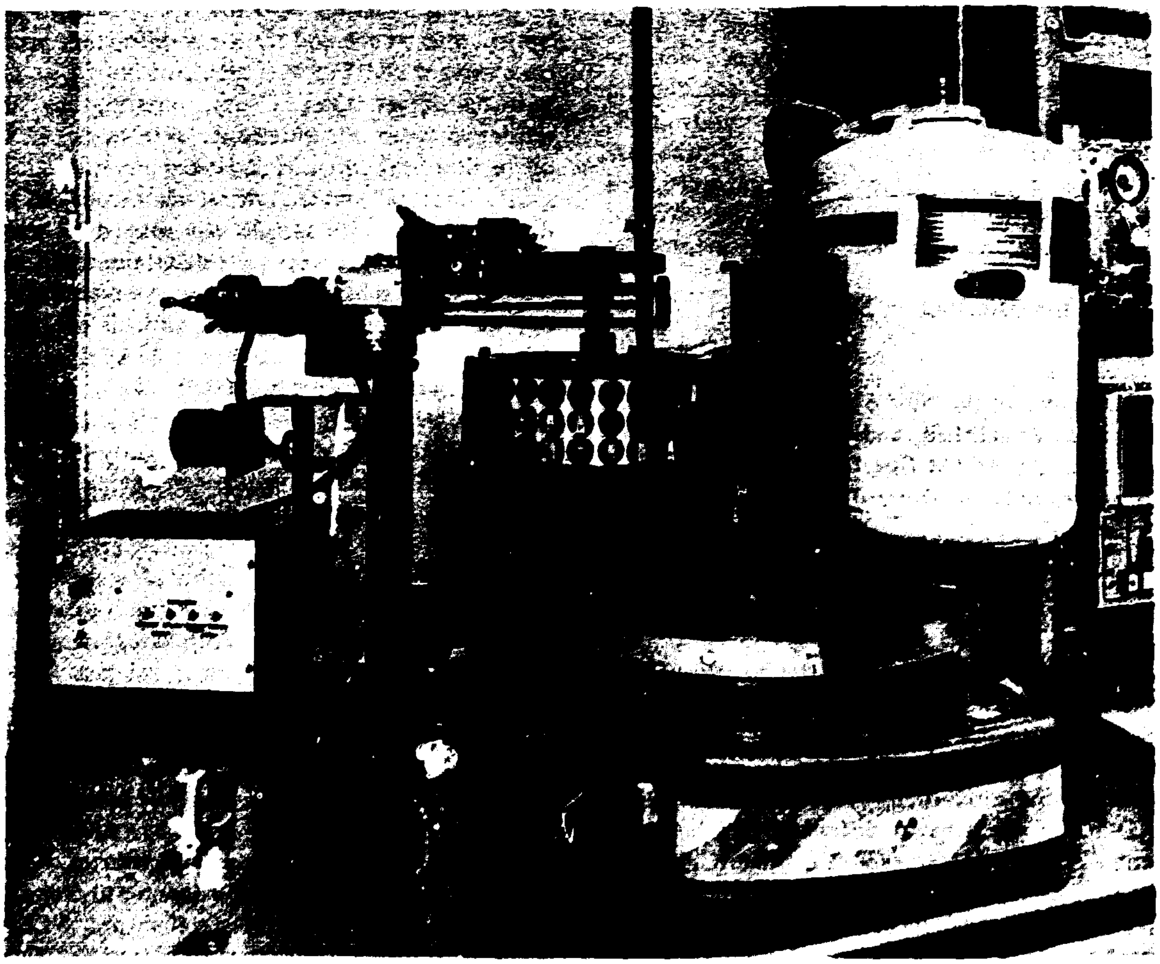

Fig. 1.3. Sample changer for XRF unit.

examine lateral or upper and lower areas of the specimens. The purpose of the goniometer is to allow variable takeoff angles between excitation source, sample, and detector.

The Chemical Technology Division (J. Begovich and R. Canon) is developing a chromatographic process for removing hafnium from zirconium. Very large numbers of solution samples of zirconium and hafnium are being generated. The automatic sample changer allows us to provide XRF service for this program. Because concentrations of zirconium and hafnium range as low as 0.1 ppm in the solutions, it is necessary to preconcentrate by coprecipitating with $Fe(OH)_3$. The concentrated samples are dried onto thin Mylar films. Because these configurations present very low scattering masses to the excitation beam, background reductions in the spectra as well as preconcentration effects are achieved. The fluorescence peak of the iron serves as an internal standard, which provides for accurate quantitation. Detection limits for zirconium and hafnium in solutions are 0.4 and 1 ppm respectively. Counting times are sufficiently short so that 160 to 180 samples per week can be processed with statistical errors of 5 to 10%. (*E. Ricci, H. W. Dunn*)

New X-ray Fluorescence Instrumentation. A unique ORNL-designed XRF analyzer system was purchased from United Scientific–Tractor Norther, Inc., on the basis of capability and competitive bidding. The TN-4000 XRF is designed for high-volume analytical support. It has multiple detectors and automated 20-position sample changers and is under computer control. A diagram of the complete XRF analyzer system is shown in Fig. 1.4. As shown, the system consists of dual Si(Li) detectors and a germanium (planar) detector system. One Si(Li) and the germanium detector system are interfaced to a containment glovebox to permit the analysis of plutonium specimens. The Si(Li) stand-alone unit is x-ray tube excited and is used for uranium and nonradioactive specimens. The Si(Li) glovebox unit has x-ray tube excitation and both ^{109}Cd and ^{241}Am isotopic excitation capability. The germanium detector unit has a ^{57}Co isotopic source to permit the detection of the K-shell energies of all rare earth elements and the K-shell emissions of uranium, plutonium, and thorium. The Si(Li) systems were both successfully tested and placed in operation. The germanium detector system is being interfaced to the glovebox for acceptance testing.

We have developed practical, routine XRF analysis methods to support several CFRP engineering studies of aqueous-organic distribution coefficients, using nonradioactive elements t[illegible]late those that would be present in dissolv[illegible]ent solutions. These XRF methods in [illegible], Zr, Ru, U-Th, and U-Zr in both mine[illegible]d TBP-dodecane solutions. We also developed a rapid analysis of synroc (a synthetic rock) mineral for seven major elements; this program supports studies of a long-term nuclear waste storage technique.

A computer program was written to permit completely automated overnight data acquisition for cost effective analysis of specimens that require lengthy analysis times.

The new XRF system has demonstrated the Analytical Chemistry Division's goal of providing rapid, accurate, low-cost technical support by

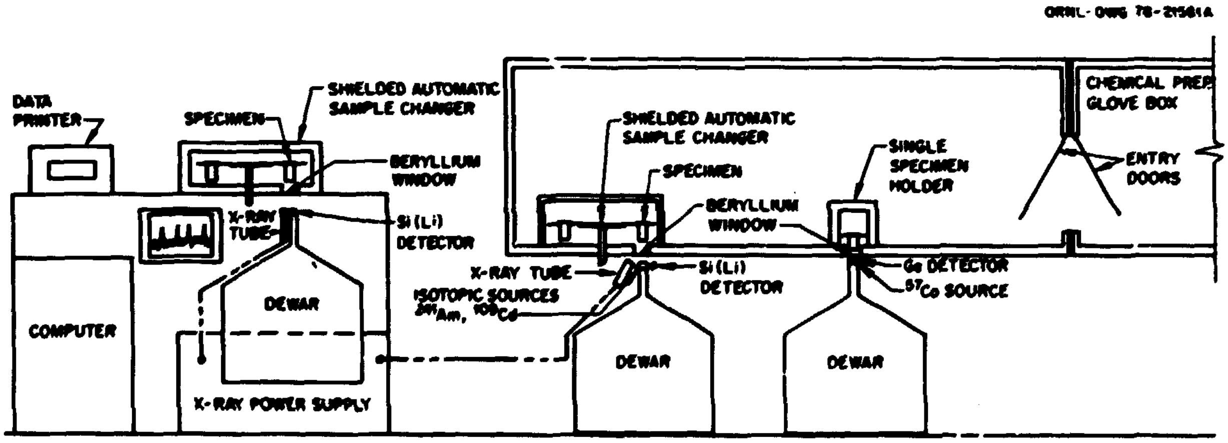

Fig. 1.4. ORNL-designed XRF analyzer system.

analyzing as many as 100 samples (for both uranium and zinc) during a single working day. (*J. H. Stewart, Jr., R. D. Brooksbank, D. A. Constanzo*)

Positron Spectroscopy

For several years it has been known that monoenergetic positrons can be generated by bombarding certain solid moderators with radioactive positron sources, such as ^{58}Co or ^{22}Na. The spectra of positrons from natural radioactive sources are broad and continuous, with energies ranging as high as 600 keV; when positrons enter solid materials, they are decelerated to very low energies, presumably thermal. If conditions within the solid and on its surface are proper, a measurable number will escape back into the vacuum without being annihilated. The spectrum of positrons moderated in such a manner usually consists of a single narrow peak with an intrinsic FWHM less than 1 eV. This suggests a principle for constructing a monoenergetic positron gun. The Physicochemical Methods Group has initiated a seed-money program to make such a gun and evaluate the practicality of positron spectroscopy for surface analysis.

We have found that tungsten and molybdenum moderators, prepared in a special manner, are highly effective for producing monoenergetic positrons. Their yields approach 10^{-3}, which is 100 times more efficient than the commonly used MgO. With a 6.5-mCi source of ^{58}Co, a count rate of 2000 monoenergetic positrons per second has been achieved. Two factors appear to be very important for developing high efficiencies: the reduction of the degree of defect structure, such as grain boundaries and dislocations, and the elimination of excess oxide and adsorbed water from the surface.

The molybdenum and tungsten moderators are prepared by heating to high temperatures in vacuum. This reduces defect structure by effecting recrystallization and grain growth and cleans surfaces by volatilizing excess oxide. The need for high crystalline perfection appears consistent with many reports that defects in metals trap thermalized positrons. X-ray photoelectron spectroscopy studies show that the surfaces of the better moderators are much less contaminated with oxygen and adsorbed water than are others. The reason for the deleterious effects of oxides and water is not clear, but perhaps they promote the trapping of thermalized positrons also.

Electrons with thermal kinetic energies are retained in metals because their potential energies are negative with respect to the vacuum level. In certain metals, however, the potential energy of thermalized positrons may be positive with respect to the vacuum level, and there is a driving force to expel the positron rather than to retain it. This has been called the negative work function, and it may also be a very important factor in determining yields of low-energy positrons. Mills[37] has recently presented experimental evidence for the negative work function; Nieminen and Hodges[38] have calculated work functions of positrons for several transition and noble metals. Tungsten and molybdenum have two of the largest values listed, −2.1 and −2.0 eV. Iridium has the next largest value, −1.7 eV, and it was found to have the third-best positron moderation efficiency. Thus, we have a very interesting correlation. Perhaps the negative work function contributes to moderation efficiency by driving thermalized positrons out of the metal before they are annihilated.

A high intensity ^{22}Na source of positrons has been purchased. With the help of the Solid State Division, single-crystal tungsten moderators are being prepared with the hope of generating even higher efficiencies. If a gun having practical intensities can be developed, it will be used for elemental analysis of surfaces by disappearance potential spectroscopy and for crystal structure measurements by low-energy positron diffraction. (*L. D. Hulett, J. M. Dale*)

Chemical Speciation of Fly Ash from Coal-Burning Steam Plants

The elemental composition of fly ash is well known. The major elements are silicon (20–35%), aluminum (5–15%), and iron (2–20%), with equivalent concentrations of oxygen. Alkali and alkaline earth metals, carbon, and sulfur are present in minor concentrations ranging from 0.1 to 3.0%. Elements that are considered as posing the largest threat to the environment, such as Pb, As, Cd, V, Cr, Co, Ni, and Cu, are present in trace concentrations of less than 1000 ppm. A knowledge of only the elemental composition is not adequate, however, to make possible an estimate of the effects of fly ash on the environment. The chemical species (compound forms, valence states) of elements is an overriding factor in determining how they escape from disposal sites and assimilate in waters, soils, and plant and animal life. The object of this work was to determine as much as possible about the chemical species of elements in fly ash.

Determining the chemical states of the major elements silicon, aluminum, and iron does not appear to be a particularly difficult task. The compound forms of these elements are sufficiently high in concentration so that molecular probes, such as XRD, Mössbauer, XPS, and infrared spectroscopies, can be applied. The species of the minor and trace elements usually cannot be determined in such a direct manner, however, because molecular spectroscopies almost invariably have limited sensitivity. It is necessary to use chemical inference. Chemical separations must be performed on the ash; the elements will respond to these treatments according to their valence and molecular forms, and atomic spectroscopies will then be used to determine how the elements become distributed into the various fractions, thus inferring their original chemical states. This is the approach that we have used on fly ash. The magnetic ferrites, spinels, and iron oxides were physically isolated from fly ash and then further purified of their sintered aluminosilicate materials by extracting in HCl. The extracted solutions, which were very rich in iron and aluminum, were analyzed by neutron activation (NAA), atomic absorption (AA), and XRF spectroscopies. Before extraction in HCl, the molecular structures of the magnetic phases were studied by XRD and Mössbauer spectroscopy. The nonmagnetic aluminosilicate materials consisted of the crystalline phases, mullite and quartz, and the amorphous glasses. The glass phases were leached with dilute (1%) HF, leaving the mullite and quartz as undissolved residues. The extracted glasses and the crystalline phases were individually analyzed by NAA, AA, and XRF. The nonmagnetic aluminosilicate material was examined by x-ray diffraction before and after the HF leach.

X-ray diffraction, Mössbauer spectroscopy, and elemental analyses showed that the magnetic phases consisted mostly of ferrites ($Fe_{2.3}Al_{0.7}O_4$) instead of the commonly reported magnetite (Fe_3O_4). The crystal symmetry and the *d*-spacings of these two compounds are very nearly the same, but high resolution measurements can distinguish them. Trace element analysis of the magnetic phases showed that they were highly enriched, by factors of 10 to 60, in the first-row transition elements, V, Cr, Mn, Co, Ni, Cu, and Zn. It is well known that these elements readily dissolve in spinel matrices, forming compounds of the type $MO{\cdot}(Fe_2O_3)$ or $FeO{\cdot}(M_2O_3)$. Thus, we have a clear inference of the chemical species of these trace elements.

The mullite-quartz residues left after the HF leach were found to be relatively pure phases. They were almost completely free of alkali, alkaline earth, and other mono- and divalent elements. Certain +3- and +4-valent elements, such as V, Cr, Fe, Ga, Ti, and Zr, were found in relatively high concentrations. Vanadium was about equally distributed in concentration between the glass and the crystal phases. Gallium was exclusively contained in the crystal phases, while chromium was concentrated by a factor of 2. These results suggest that those trace elements in the crystal phases are contained as isomorphic substitutions for aluminum and silicon. Figure 1.5 shows scanning electron micrographs of mullite and quartz residues left after the glass phases were removed. The aggregates of acicular crystals in Fig. 1.5 (*a*, *b*, and *c*) reflect the spherical forms of the fly-ash particles before etching. As the molten droplet solidified, the crystals nucleated from its surface and grew inward to interlace the interior. The glass phases were frozen out and occupied the interstitial positions between the needles.

In the nonmagnetic portions of fly ash, the majority of the trace elements occur in the glass phases. Arsenic, lead, cadmium, rare earths, and alkali and alkaline earth metals are apparently excluded from the mullite and quartz phases as they solidify and are forced to concentrate in the glasses. Further studies must be done to describe the chemical states of these trace elements more explicitly, but even though we cannot say exactly "what" they are, we have at least determined where they reside — in the glass phases. We are also able to say that the chemical potentials of these elements, with regard to their propensities to escape, are higher than gross element analyses indicate, because they are concentrated in a single phase.

Practical conclusions pertaining to both pollution abatement and resource recovery can be drawn from this work and immediately implemented. (1) The magnetic phases from fly ash could be reduced before the ash is placed in disposal sites; this action would reduce leaching of V, Cr, Mn, Co, Ni, Cu, and Zn. (2) The mullite-quartz phase is high purity and could be isolated and used in the manufacture of refractory ceramics. (*L. D. Hulett, A. J. Weinberger*)

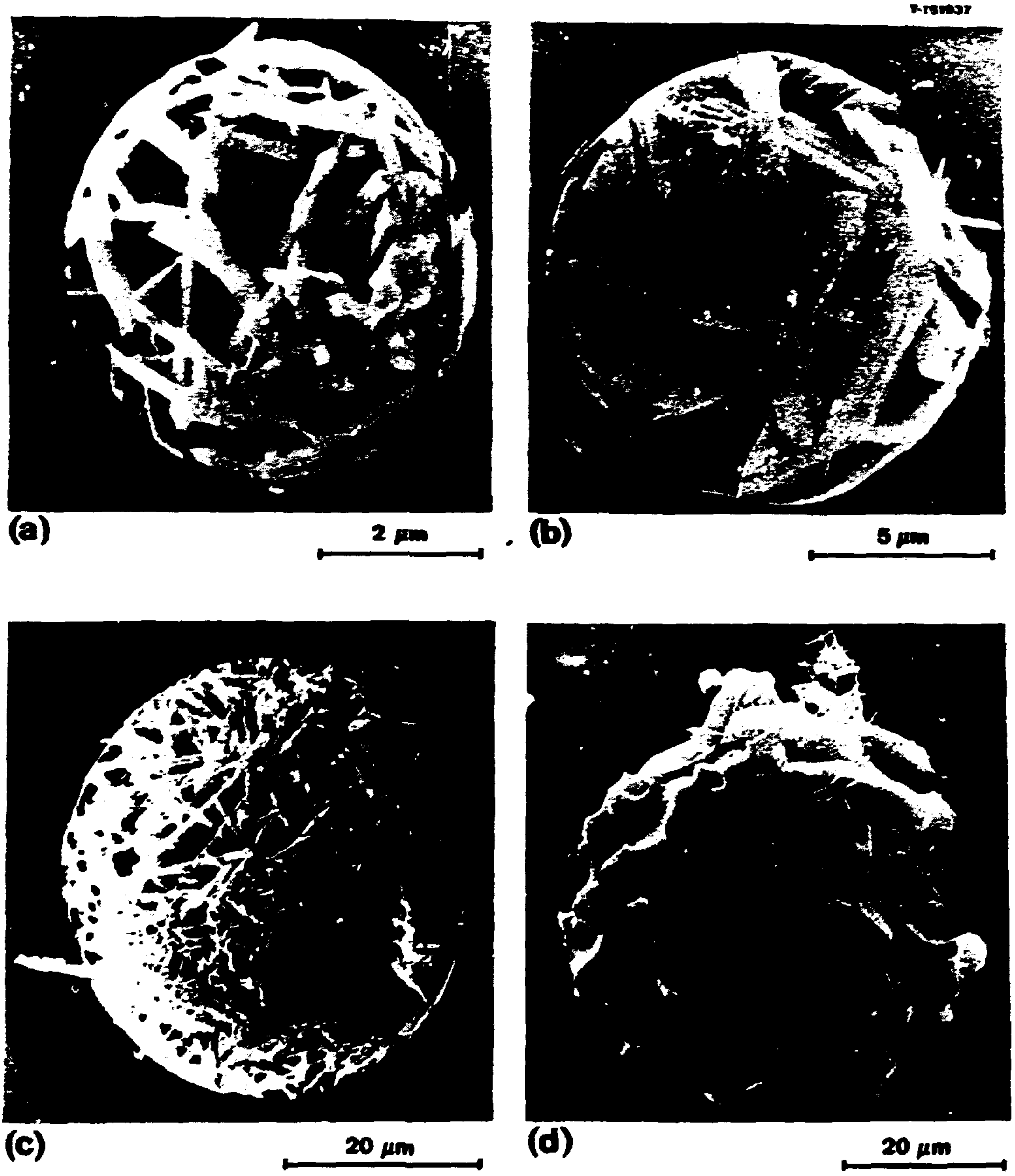

Fig. 1.5. Scanning electron micrographs of skeletons of fly-ash particles remaining after etching in 1% HF: HF: (*a*), (*b*), and (*c*) show aggregates of mullite crystallites; (*d*) is a quartz particle.

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2. Mass and Emission Spectrometry

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R. L. Walker, Associate

The Mass and Emission Spectrometry section in serving an energy-related clientele operates a variety of expensive spectrometers, sophisticated and sensitive, for the measurement of inorganic and organic constituents. The section's activities for this reporting period are divided into three groups: Organic Mass Spectrometry, Inorganic Mass Spectrometry, and Elemental and Ion Probe Surface Spectroscopy. DOE-funded research and development activities are described in each subdivision of this report, along with important technical support activities.

Construction of the three-sector high-resolution mass spectrometer mass spectrometer (MSMS) system has been completed, and it is being used for organic mass spectrometry research. This unique instrument is advantageous because of (1) the wide range of metastable ion scan modes possible in a single instrument, (2) its adaptability to field ionization kinetic studies, (3) its use for photon or laser-induced ion dissociation studies, and (4) its utilization for the study of ion lifetimes (1 to 60 μs). These various modes of operation make the instrument especially useful in the analysis of complex isomer mixtures. Fence-line samples from the Gulf Coast area, taken by EPA on Tenax polymer, have been analyzed by a gas chromatograph mass spectrometer (GCMS). Over 150 different organic compounds have been identified from the heavily industrialized area. Quantitative measurements are also being investigated by the use of internal standards fixed on the Tenax.

During this year, the section oversaw the installation and checkout of two mass spectrometers. One is a time-of-flight instrument (Metals and Ceramics Division) used for gas analysis of irradiated fuel particles, and the other is a ratio mass spectrometer for ^{15}N measurements (Environmental Sciences Division).

Work has begun on the replacement of obsolete multichannel analyzers for our two-stage isotope-ratio mass spectrometers. Two minicomputers, acting as remote stations for a PDP-11/34, will be employed for instrument control and data collection. A sensitive isotope dilution method has been developed for the analysis of ^{99}Tc in environmental samples. Calibration of the ^{97}Tc spike material for use in the method has been complete Minor isotopes measurement campaigns on several enrichment cascades have also been completed.

The spark source mass spectrometer to be used for analysis of highly radioactive samples has been checked out for cold operation. The Engineering Division completed the design of remote manipulation and shielding for the instrument, and final construction and installation is under way in cell 6 at Building 2026.

A cesium ion source has been built, and the first prototype used on the ion microprobe mass analyzer for generating enhanced signals from electronegative elements. The cesium source will permit depth profiling of *n*-type implanted dopants in solar cell devices. The ion microprobe has been interfaced to a PDP-11 34 computer for real-time data acquisition and processing. Ion implantation has been used as a precise method for preparing standards to calibrate a spark-source mass spectrometry (SSMS) for near-surface region analysis.

Samples from the Three Mile Island reactor site were analyzed for uranium and plutonium by isotope dilution mass spectrometric techniques. Boron, lithium, and a host of other elements were also analyzed by SSMS.

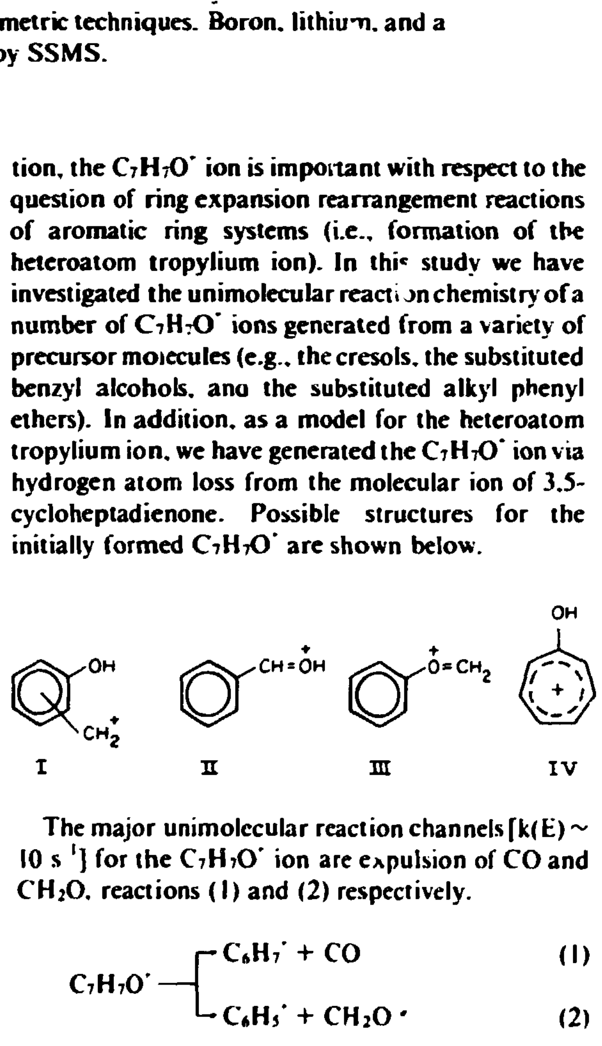
ORGANIC MASS SPECTROMETRY

The basic research program for the organic mass spectrometry group encompasses three areas of investigation, that is, the chemistry of gas-phase ions (unimolecular and bimolecular), the development of experimental techniques for deducing ion structure, and the development of new ionization methods.

Ion Chemistry

Because the chemistry of gas-phase ions is very much dependent on the internal energy of the ion, it is often difficult to make a direct comparison of experimental data obtained by different techniques. For this reason, the major portion of our ion chemistry studies utilizes reactions that occur within the field-free regions of the mass spectrometer (i.e., metastable ions). The lifetime for a metastable ion, and thus the average internal energy of the ion, is much better defined than it is for reactions that occur within the ion source. In addition, the unimolecular dissociation of metastable ions is attributable to ions that are formed initially with low internal energies, thus minimizing the possibility for structural rearrangement. Another desirable aspect for employing metastable ions for the study of ion chemistry and for analytical studies is that unambiguous assignment of the reaction sequence is possible by use of the appropriate scanning modes. Furthermore, the fraction of the internal energy that is converted into energy of translation (i.e., metastable kinetic energy release) can be accurately measured by most metastable ion scanning methods. This quantity has significance for both fundamental and analytical applications.

During the past year, we have utilized metastable ion techniques for a systematic investigation of the $C_7H_7O^+$ ion. The $C_7H_7O^+$ ion is an important secondary ion in the mass spectra of a variety of oxygen-containing aromatic compounds. In addition, the $C_7H_7O^+$ ion is important with respect to the question of ring expansion rearrangement reactions of aromatic ring systems (i.e., formation of the heteroatom tropylium ion). In this study we have investigated the unimolecular reaction chemistry of a number of $C_7H_7O^+$ ions generated from a variety of precursor molecules (e.g., the cresols, the substituted benzyl alcohols, and the substituted alkyl phenyl ethers). In addition, as a model for the heteroatom tropylium ion, we have generated the $C_7H_7O^+$ ion via hydrogen atom loss from the molecular ion of 3,5-cycloheptadienone. Possible structures for the initially formed $C_7H_7O^+$ are shown below.



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The major unimolecular reaction channels $[k(E) \sim 10\ s^{-1}]$ for the $C_7H_7O^+$ ion are expulsion of CO and CH_2O, reactions (1) and (2) respectively.

$$C_7H_7O^+ \left\{ \begin{array}{ll} \rightarrow C_6H_7^+ + CO & (1) \\ \rightarrow C_6H_5^+ + CH_2O\cdot & (2) \end{array} \right.$$

Typical branching ratios for reactions (1) and (2) are listed in Table 2.1. Although there are considerable differences for the branching ratios for the various $C_7H_7O^+$ ions, it is difficult to ascertain the reason(s) for these differences. However, results for metastable kinetic energy (KE) release measurements are consistent with different structures for the decomposing $C_7H_7O^+$ ions. We interpret these metastable branching ratios and metastable KE release values as unique structural forms for decomposing $C_7H_7O^+$ ions (structures I–IV). However, these experimental

Table 2.1. Decomposition values of $C_7H_7O^+$ ions from various compounds

Parent compound	Reaction 1		Reaction 2	
	KE release	Branching ratio	KE release	Branching ratio
m-chloroanisole	20 300[a]	95[b]	30[a]	5[b]
p-chloroanisole	25 300	75	25	25
2-phenoxyethanol	20 275	95	20	20
m-chlorobenzylalcohol	195	99		1
p-chlorobenzylalcohol	195	99		1
1,2-diphenylethanol	185	99.8		0.2
o-cresol	350	90	120	10
m-cresol	410	65	140	35
p-cresol	470	60	170	40
3,5-cycloheptadienone	390 930	90	140	10

[a] Metastable KE release expressed in millielectron volts.

[b] Metastable branching ratios expressed as percentage of total metastable ion current.

results leave unanswered the question of why $C_7H_7O^+$ ions, formed initially as III and IV, give rise to composite metastable peak shapes. Additional experiments are under way to explore further the mechanism for decomposition of $C_7H_7O^+$ ions.

Although the KE release and abundance ratio data for the C_7H_7O ion clearly establish four distinct structures, it is desirable to develop more specific methods for the identification of ion structure. Consequently, new instrument types and experimental methods have been developed in an effort to extend the capabilities of mass spectrometry for chemical analysis. In the area of organic mass spectrometry, a major achievement was the introduction of the reversed-geometry or mass-analyzed ion kinetic energy spectrometer (MIKES).

Design and Testing of a Three-Sector Spectrometer

We have recently completed the design, construction, and performance evaluation of a three-sector mass spectrometer (electric sector/magnet/electric sector). The three-sector configuration is ideally suited for both fundamental and analytical studies of metastable ions. Unimolecular or collision-induced dissociation reactions occurring in the first, second, or third field-free regions may be investigated by conventional defocused scan methods, that is, accelerating voltage scans (HV), combined magnet/second electric sector scans (B/E or B^2/E), and second electric sector scans (MIKES) respectively.

The basic double-focusing mass spectrometer, electric sector I and magnet, was designed and constructed at ORNL. The instrument has partial second-order double focusing and has achieved a mass resolution of approximately 30,000. The second electric sector was added to the original instrument and is of the same design as electric sector I, with a 43.25-cm radius and a deflection angle of 90°. The image and object focal points (l_{e2} and l_{oe2}) for the second electric sector were calculated by the Hintenberger method[1] and give first-order direction focusing. Thus, the mass separation device (electric sector I and magnet) maintains the partial second-order double-focusing characteristics necessary to achieve high mass resolution.

The large radii of the electric sectors (43.25 cm) is important if one wishes to perform high energy-resolution measurements. To date, the instrument has achieved about 5000 energy resolution with adequate sensitivity for single-scan metastable data acquisition. In addition, the focusing characteristics of the instrument give good peak shapes for composite and dish-shaped metastable peaks. We have measured the KE release for a large number of unimolecular decompositions in the first and third field-free regions, and we find good agreement with published data.

The unique feature of the three-sector configuration is that the double-focusing section of the instrument (electric sector I and magnet) can be operated in the high mass resolution mode and a metastable spectra of the mass-separated components obtained via MIKES scans. This mode of operation would be of particular importance for mixture analysis where sample separation via classical methods is not practical. This type of experiment is analogous to capillary column GCMS; the high-resolution component separation device is now a high-resolution mass spectrometer instead of a capillary column GC. We have successfully demonstrated this mode of operation by obtaining a metastable spectra for each of the mass-resolved components at mass to charge ratio (m/z) 79 ($^{13}CC_5H_6$ and $C_5H_5{}^{15}N$ in a benzene/pyridine mixture (90% benzene). The resolving power employed for the experiment was about 14,000.

The instrument is currently being used to investigate the chemical properties and unimolecular decomposition reactions of gas-phase ionic systems. A complete description of the instrument will be published in the *International Journal of Mass Spectrometry and Ion Physics*. (*D. H. Russell, D. H. Smith, R. J. Warmack, W. T. Rainey, T. R. Mueller*)

KRATOS MS-50/DS-50 Modifications

Several projects, now in the planning stages, require high-resolution computer data acquisition and analyses. These projects are (1) a definitive evaluation of GCMS vs MSMS techniques on "real" complex mixtures, (2) medium resolution (~5000) capillary column GCMS evaluation, and (3) the utility of high-resolution GCMS as a support activity for low resolution GCMS. Several instrumental requirements were needed for these tasks. The GCMS interface was modified to allow direct (no split) GC effluent flow to the MS for capillary column work. A second disk drive and support software were installed to allow greatly expanded (~1 megaword) disk storage for repetitively scanned data storage. The second disk also allows immediate rebuilding of backup disks with processing software. Circuitry for B/E scans has been installed in the metastable unit of the MS-50. It will be used in conjunction with a new KRATOS mass marker. The B/E scan mode will be used to assess the MSMS capabilities of the MS-50. Reliability of the overall DS-50 data system is being improved by addition of new I/O hardware and reconfiguration of old I/O hardware to allow the VDU terminal and DECwriter to be accessed by individual device codes. This configuration will then be "standard" for KRATOS factory representatives and will simplify repair. (*D. C. Canada, W. T. Rainey, E. H. McBay, L. K. Bertram*)

Alternate Ionization Methods

To further increase the capabilities of mass spectrometry for chemical analysis, new methods for ion production are needed. Conventional mass spectrometry is limited by the requirement of sample vaporization prior to ionization of the sample. At present, the limitation of sample evaporation may be overcome by field desorption ionization and by plasma desorption mass spectrometry (PDMS) of a solid sample. These methods are undesirable because of poor reproducibility, low sensitivity, and the limited number of organic substrates amenable to these ionization methods.

We have recently initiated a study to evaluate the potential of our ion microprobe mass spectrometer (IMMA) for mass spectral studies of nonvolatile organic and organo-metallic substances. The ion microprobe is especially suited for these studies, due to high sensitivity, ability to select a large variety of ionizing reagents, and the ability to control primary ion (ionizing reagent gas) energy. Initial work was performed with Ar^+ at 15-keV impact energy, and preliminary results are very encouraging. Abundant secondary ion current was produced that corresponded to a cationized organic species (the organic molecule plus a metal atom from the supporting surface) followed by fragmentation of the cationized organic substrate. The fragment ions observed were analogous to those observed in conventional electron impact and chemical ionization mass spectrometry. Additional experiments are planned to test the proposed fragmentation schemes observed in these preliminary experiments. We plan additional, subsequent experiments to investigate the secondary ion yield as a function of primary ion energy and the effect of adding other cationizing species.

Previous studies on thermal translational energy ions, such as those formed via electron impact ionization within the cell of an ion cyclotron resonance spectrometer (ICR), have demonstrated a large absorption cross section for isolated gas-phase organic ions in the visible and ultraviolet region. Accordingly, we have begun to investigate photon-induced dissociation or photofragment spectroscopy (PFS).

In our experiments, ions are produced via electron-impact ionization in the source of a three-sector MIKE spectrometer. The ion of interest is mass selected by the double-focusing mass spectrometer, and fragment ions formed in the third field-free region are analyzed via conventional MIKE scans. In the third field-free region, a photon beam is crossed perpendicular to the mass-analyzed ion beam. The photon beam is supplied via a 2.5-kW Hg/Xe arc lamp. The fragment ions formed as a result of photon activation are mass analyzed via the second electric sector. Strictly speaking, the second electric sector is a kinetic energy analyzer that can be calibrated in mass units.

To date we have performed PFS studies on two chemical systems, the molecular ion of benzyl chloride and $C_7H_7^+$ formed via Cl-loss from the benzyl chloride molecular ion. The products of photon excitation are the same as those previously reported from ICR studies, reactions (3) and (4).

$$C_7H_7Cl^{+} \xrightarrow{h\nu} C_7H_7^{+} + Cl\cdot \qquad (3)$$

$$C_7H_7^{+} \xrightarrow{h\nu} C_5H_5^{+} + C_2H_2 \qquad (4)$$

For reaction (3), the signal enhancement above the normal metastable reaction background was approximately a factor of 3; for reaction (4), the enhancement was only 1.4. The reason for the considerable difference for the observed signal enhancement is that the dissociation maximum for $C_7H_7^+$ ions is 280 nm, a region of low photon flux for the Hg Xe light source, whereas reaction (3) occurs from two absorption maxima, 400 and 560 nm. Nevertheless, these experiments establish the feasibility for performing PFS via MIKE spectrometry and warrant additional studies. (*D. H. Russell, W. H. Christie*)

Organic Mass Spectrometry Support Work

The Organic Mass Spectrometry group has given support to a wide variety of programs throughout the three-plant area in qualitative organic analysis of complex mixtures. Considerable effort was applied to problems in collaboration with investigators in the Analytical Chemistry Division, and also with those from Chemistry, Biology, Health and Safety Research, and Plant and Engineering. In addition, the collaborative project with the Environmental Monitoring and Support Laboratory (EMSL) of EPA on characterization of air quality in the industrialized area of the Gulf of Mexico has been a major portion of the work.

The DuPont 490B spectrometer has been used for most of the support work, since acquisition and processing of data are handled by the data system. Because of the complex nature of many samples, rather long chromatographic runs (2–4 h) have been necessary, resulting in tremendous quantities of data acquired while repetitively scanning the spectrometer. The versatility of the data system allowed processing of the data in reasonable times, which had been impossible with manual processing. For instance, we performed for C.-h. Ho of the Analytical Chemistry Division analyses of components in basic fractions of amines and cyclic nitrogen compounds derived from shale oil, synthoil, and coal gasification products. These analyses required long chromatographic runs, but they yielded corroborative and unambiguous identifications, which have been of value to the programs. Interpretative techniques, as well as automated library searching and mass chromatographic searching, were used to assist in the analyses.

We have rendered assistance to Plant and Equipment personnel in their program to reorganize waste disposal areas by identifying the contents of drums of unknown chemicals. It is planned to combine similar, and compatible, materials into large and more permanent containers for storage. Analysis of individual batches is necessary prior to any such combination, although most of the drums contained Amsco-TBP mixture from processing runs and were suitable for combination in storage tanks.

We have also assisted F. F. Knapp and other coworkers in the Health and Safety Research Division by the identification of a variety of metal-organic compounds synthesized by them for nuclear medicine studies. Starting materials and intermediates, as well as the final products, have been analyzed by the direct inlet probe technique to ensure quality of the product. Among the most interesting compounds analyzed was a series of tin-barbiturates and telluro-steroids, compounds previously unknown.

Our collaborative project with EMSL on studies of air quality in the Gulf area is continuing. Development of techniques and instrumentation has been carried out under the supervision of E. Pellazzari of the Research Triangle Institute (RTI).

The primary purposes of the pilot studies have been (1) to furnish fence-line data on all identifiable pollutants, (2) to assess the state-of-the-art techniques for monitoring air quality, and (3) to assess the quality assurance plan proposed for such projects. The participation of the three laboratories has resulted in a large data bank, as well as a better assessment of the program. It has been encouraging that the results have been in very good agreement and that the quality assurance program seems adequate.

Tenax cartridges were prepared at RTI under carefully controlled conditions that ensured cleanliness and reproducibility. Air sampling was done by EPA personnel under selected and recorded conditions at several sites: Lake Charles, Louisiana, and Beaumont and Houston, Texas. Each participating laboratory was given the major analysis task for one of the sites; the other laboratories were given duplicates of selected cartridges. Blank cartridges were always carried through shipping and handling operations as controls to detect contamination or instability problems. Selected cartridges were also spiked at RTI with a variety of organic compounds (in known amounts) to allow determination of relative response factors for quantitative analyses. Each cartridge was also spiked at EMSL after sampling, with known amounts of perfluorobenzene (PFB) and perfluorotoluene (PFT) to assist in quantitative analyses. These compounds were selected because of their low probability as air pollutants. Although their gas chromatographic retention times prevented complete separation from other organic pollutants, mass chromatographic techniques permitted adequate separation from interfering compounds.

The Nutech desorber was interfaced to the PE 3920 GC, used with the DuPont 490B GCMS system, and was operated as previously described.[2] An SP 2100 SCOT chromatographic column was used for all analyses. The measured efficiency for the system was about 45,000 theoretical plates, using methyl esters. We used a carrier rate of 2 ml min with a makeup flow at the column exit of about 7 to 8 ml min; the makeup flow was adjusted to cause about 10% of the total flow to be split and directed to the flame detector. Injection of a sample into the chromatograph was carried out with the column at 25–30°C, after which programming was started. The effluent from the GC was interfaced to the mass spectrometer through the single-stage jet separator. Data acquisition was made until the column temperature reached 250°C. Processing of data involved library searching, interpretative reasoning, and comparison with available compilations.

We have completed data acquisition from all samples and are proceeding with data processing. All data from the Beaumont and Houston samples are stored on disks. We have completed qualitative identifications from all samples and are planning to start quantitative measurements in the near future. The Lake Charles, Louisiana, samples were too old before they were analyzed to be of quantitative value, so those data were used only for qualitative information.

Approximately 150 components have been identified from these samples. Due to the similar nature of the industries in the various sites, there is great similarity in the qualitative data. The major components were aliphatic and aromatic hydrocarbons. Aliphatics from C_4 to C_{15} were identified, and benzene and naphthalene with alkyl derivatives were the aromatics found. Several chloro- and chlorofluoromethanes, and -ethanes, bromoform, alkyl phenols, and phthalate esters were the unusual species detected. Interlaboratory comparison of data from the Lake Charles study showed about 85% agreement in compound identification. This is a very satisfactory correlation, considering the differences in instrumentation, techniques, and especially, the age of the samples. (*W. T. Rainey and C. A. Pritchard*)

Evolution of Gases from Coal Samples at Temperatures <370°C

Samples of eastern and western coal were crushed under vacuum and heated to different temperatures; the evolved gases were studied by use of an analytical gas mass spectrometer. The coal samples were weighed and placed in a sample crusher and evacuated to $<5 \times 10^{-2}$ torr. The crusher was isolated under vacuum for ~18 h at 22°C, and the evolved gases from each sample were analyzed by analytical gas mass spectrometer. The crusher was again evacuated and isolated; the samples were crushed; and, after ~18 h, the gases were again studied. A temperature program was initiated and followed. The crusher was evacuated and isolated; a new temperature setting was made and allowed to come to equilibrium 18 h at the new setting; then the total evolved gases were expanded into the manifold; and a pressure-volume determination was recorded. A mass spectrometric analysis of the gases was made, and now the coal sample was ready to be taken through the next temperature step.

A background spectrum was recorded before each gas sampling and subtracted from the gross peak height to produce the net peak heights representing the sample. Principal gases in the background were from air, and there were trace hydrocarbons resulting from pump oil and fingerprints. Hydrogen cannot be satisfactorily quantified by mass spectrometry in the presence of large amounts of water. The major component found in the gases from these samples was water. There was essentially no difference in the composition of the gases from uncrushed and crushed coal at ambient temperature. Between the temperatures of 22 and 180°C, there was an increase in the amount of CO_2 and CO and only a slight increase in m/z 15, which is a hydrocarbon (possibly methane). Above 200°C, both the western and the eastern coal began to evolve higher hydrocarbons. At 210°C, the eastern coal had seven hydrocarbon masses between m/z 44 and 88; at 262°C the western coal had only two, m/z 50 and 78. At 368°C, the eastern coal had 81 hydrocarbon masses between m/z 44 and 140, plus others too small to measure. At 314°C, the western coal had 47 hydrocarbon masses between m/z 44 and 139. No unambiguous identifications of compounds can be made from these data. However, the presence of certain ions is indicative of compound types. The series of C_nH_{2n+1} and C_nH_{2n-1} (m/z 41, 43, etc.) is indicative of aliphatic substituents but may be derived from many compound types. The m/z 9, 65, 77, 41, and 39 are good indication of aromatic structures, and these fragments arise from aliphatic substituted benzenes, C_3-benzenes at m/z 120, C_2-benzene at 106, and toluene of 92. Although the list of ions detected is long, the quantity of gas evolved is small, that is, typically, Σ gas at 180°C = 0.47 m^3/t (STP). (*J. R. Walton, W. T. Rainey, J. A. Carter*)

INORGANIC MASS SPECTROMETRY

Mass Spectrometry of Plutonium, Uranium, and Thorium in Spent Fuel Solutions

Mass spectrometric methods for the determination of plutonium, uranium, and thorium have been developed by use of the resin bead technique of sample preparation and the two-stage, 30-cm-radius mass spectrometer for mass analysis.[3] The methods have been applied to the isotopic characterization and isotope dilution measurement of the amount of plutonium and uranium in high burnup, highly irradiated Robinson-Light Water Reactor (LWR) fuel. Highly enriched (98 to 99%) ^{233}U and ^{242}Pu tracers were used for the isotope dilution determinations.

Isotopic results from this work indicate that a precision of ±0.5% is obtained for minor isotopes in the 1% concentration range and ±0.1% for major isotopes in the 50 to 99% range. Analyses of synthetic dissolver solutions over a period of several months show that the uncertainty of the isotope dilution measurement of plutonium and uranium is <0.5% with precisions of 0.9% for plutonium and 0.6% for uranium.

In addition to determining plutonium and uranium, a tentative method for determining thorium has been developed and evaluated on "cold" synthetic standards and samples with ^{230}Th as tracer for the isotope dilution measurement. The use of ^{236}U as tracer when analyzing samples containing appreciable ^{233}U from the thorium-uranium fuels is proposed. (*R. L. Walker, W. R. Musick, D. H. Smith, L. K. Bertram*)

Three Mile Island

Uranium and plutonium concentrations in the Three Mile Island primary-water-loop sample were determined by mass spectrometry, along with their isotopic concentrations. The resin bead technique was exploited in the plutonium analysis. There was only about 0.015 ng of plutonium in the aliquot we received, which gave a concentration of 0.001 ng (1 pg) per bead. We thus obtained isotopic compositions on quantities too small to be analyzed by other techniques. Our results are presented in Table 2.2; also listed are expected values calculated via the ORIGEN computer code. Agreement is excellent and clearly shows that the cooling water had been in contact with the reactor core.

Table 2.2. Isotopic concentration and composition of uranium and plutonium in Three Mile Island samples

Isotope	Expected after 35-d cooling[a]	ORNL results
	Uranium (at. %)	
	(concentration 110 ppb, ^{233}U spike, solution loading)	
234	0.023	0.021
235	2.164	2.22
236	0.071	0.072
238	97.741	97.69
	Plutonium (at. %)	
	(concentration 0.24 ppb, ^{242}Pu spike, resin bead technique)	
238	0.037	<0.1
239	90.682	90.3
240	7.862	7.8
241	1.376	1.8
242	0.044	0.1

[a] Theoretical, as computed by the ORIGEN code.

Additional samples of the water in the reactor core containment vessel were taken at three levels. Analyses of these solutions were performed by various sections of the Analytical Chemistry Division. Our analyses on these samples included thermal emission mass spectrometric analysis of uranium and plutonium for quantity and for isotopic composition; spark source and ion microprobe analyses for isotopic composition and quantities of lithium and boron were also done. Good agreement was obtained in the results of the latter two techniques. The results have been summarized and reported. (*J. A. Carter, R. L. Walker, D. H. Smith, W. H. Christie, R. E. Eby, L. Landau, W. R. Musick, H. C. Smith, E. G. Miller*)

^{99}Tc by Isotope Dilution Mass Spectrometry

The development of an isotope dilution method for ^{99}Tc has been completed during the past year. The method employs the resin bead loading technique for filament loading and ^{97}Tc as the isotope spike. The ionization efficiency of technetium is approximately 50 times greater when loaded on anion resin beads than when loaded as a solution. The limit of detection is 0.1 to 0.2 pg and is near the expected limit, due to uncertainties caused by hydrocarbon interference and interference caused by molybdenum in the rhenium filaments at the mass 97 position.

Approximately 2 μg of ^{97}Tc were made in the HFIR by irradiating 25 mg of isotopically enriched ^{96}Ru for 20 d at a neutron flux of 6×10^{14} neutrons $cm^{-2}\ s^{-1}$. Half of the target has been retained for future use. The yield from the processed target was 1.6 μg and had the following isotopic composition.

Mass	At. % ± standard deviation
97	79.642 ± 0.097
98	20.175 ± 0.100
99	0.183 ± 0.006

This is enough spike to run several hundred samples by the use of a recommended spike containing 1 ng per sample. We were surprised to find the high ^{98}Tc and ^{99}Tc content in the products; however, the amount of ^{99}Tc in the spike will not affect its usefulness, except that the ultimate sensitivity is significantly reduced. Assuming the contribution of the sample (^{99}Tc) to be 20% greater than the spike, the detection limit would be about 0.2 pg. (*R. L. Walker, E. G. Miller, H. C. Smith*)

Channel Electron Multiplier Array Detector for Spark Source Mass Spectrometry

Evaluation of the channel electron multiplier array (CEMA) detector for SSMS is complete. Various optical detectors were tested, including a silicon-vidicon television camera, a linear diode array, and a photomultiplier tube. A signal averager was used to accumulate the data and correct for background, significantly increasing the signal-to-noise ratio.

Quantitative data were obtained on three types of sample to assess the system's versatility and potential. Indium was analyzed quantitatively by the isotopic dilution technique; fly ash was analyzed for six elements, using a method in which separated isotopes were taken to be internal standards; and a Zr/Hf system was studied to determine whether or not interelement measurements would be feasible.

The results of these experiments showed that the CEMA has potential for substantially better performance than is presently available. Improvements in linear dynamic range and spatial resolution of CEMA are required before it will supplant photoplates and multipliers or will be brought into routine use. Two publications of this work have been submitted to the *Journal of Mass Spectrometry and Ion Physics*. (*D. L. Donohue, J. A. Carter, G. Mamantov*)

Analysis of Fission Gas Inventories of High-Temperature Gas-Cooled Reactor Fuel Particles

The Bendix MA-3 time-of-flight mass spectrometer (TOFMS) has been attached to the particle crushing facility designed by personnel of the Metals and Ceramics Division and has been used to analyze the fission gas content of a variety of irradiated high-temperature gas-cooled reactor (HTGR) fuel particles. Several instrumental modifications have improved the precision of data and the ease of operation. The original cooling system, which used a mechanical Freon refrigerator to cool both the mercury diffusion pump and the high vacuum baffle, was rebuilt to allow water cooling of the diffusion pump. Much lower and more constant background has resulted, allowing greater precision and accuracy in data, especially from low-level components. In cooperation with personnel of the Instrumentation and Controls Division, a Data System DSD-220-RX02 compatible dual, double-density disk drive has been added to the PDP-8 data system. Programs in FOCAL are now available for the determination of mass selection voltages, calibration, data acquisition and processing, and output.

Selection of the masses to be sampled is made by varying the delay of the anode gating pulse. Software is available for stepping the delay over a mass range containing the desired mass. Visual selection of the decay resulting in the maximum signal and introduction of that delay into the acquisition program allows "peak hopping" through a series of selected masses for quantitative measurements.

Calibration for quantitative measurements is performed by introducing bursts of known gas mixtures into the particle-breaking chamber while acquiring data. Software is available for construction of the calibration curve that is to be used for interpolation with unknown samples. Several calibration volumes have been used because of the wide range of fission gas volumes contained in the irradiated fuel particles. Due to the low abundance of ^{136}Xe in natural xenon, calibration of ^{136}Xe was poor. However, the use of a standard mixture of fission-produced xenon in krypton has permitted satisfactory calibration for all isotopes found as fission products.

The acquisition program is capable of "peak hopping" through a series of 15 different masses at a reproducible rate. Each mass is sampled a preset number of times, each sample being an integration of the ion count for a preset time, before stepping to the next mass. The multiple samples taken at each mass position are averaged for use in processing. Repetitive scans are acquired for the duration of the gas pulse. In actual practice, the scanning is started prior to sample introduction to allow accumulation of background data, which is used for subtraction.

Data may be output in a variety of formats for checking the original integrated data, averaging, background counts, and for off-scale peaks. Analyses of known volumes of standard mixtures have given results showing maximum variations of about 5%. The inherent electronic noise of the system appears as background and limits, with reasonable accuracy and precision, the sample size that can be analyzed. The gas content of irradiated particles is well above this noise level.

Data from crushed particles are insufficient for statistical analysis, although burn-up calculations furnish theoretical yields of xenon and krypton. Some variations in data have been observed, and since reproducibility of analyses of known gas volumes has been good, the variations may be due to imperfections in particle coating layers. Work is continuing on the irradiated fuel particle analysis and will be extended to include measurements of helium and neon permeation rates in particles. (*W. T. Rainey*)

Mass Spectrometry Research and Development for Safeguards

In various stages in the nuclear fuel cycle, significant progress has been made this year in our efforts to demonstrate the utility of the resin bead uranium and plutonium sample loading technique as a viable analytical tool for international and domestic safeguards. This year we completed a demonstration of the compatibility of the resin bead technique and single-stage mass spectrometers; this work has been published.[4]

A quadrupole mass spectrometer has been ordered from Pernicka Associates, Sunnyvale, California. We will assess its utility as an onsite analytical instrument to make relatively crude (±1%) isotopic ratio measurements. A quadrupole has never been used in this application before; therefore, its ability is largely unknown.

We have participated in the Safeguards Analytical Laboratory Evaluation (SALE) program and have analyzed UO_2 for content and isotopic composition. We have obtained reasonable agreement with consensus values, our results on the second batch of samples being better than those for the first. The reason for this is our development of the revised mass spectrometric procedures described in the next section. The purpose of participation in this program is to verify the validity of our own procedures and to document the results for comparison of methods.

We received part of two DEC MINC data systems that will serve as data collection devices for our multistage mass spectrometers. The units themselves are here, but the peripherals necessary for communication to the outside world have not yet arrived. When the entire system is assembled, two or three satellite stations (the MINCs) will communicate with the central PDP-11/34 via DECnet. The control computer will perform all data processing operations. (*D. H. Smith, J. A. Carter, R. L. Walker, T. R. Mueller, H. Simmons, E. G. Miller*)

Projects for the International Safeguards Projects office. Two Japanese scientists, K. Kagami and S. Irinouchi, spent five weeks with us learning the resin bead technique. When they returned to Japan, they sampled five spent-fuel dissolver solutions, using the new technique, and shipped the samples to us on resin beads. All beads were received intact, but our results indicate problems somewhere at the Japanese end. We are currently trying to clarify this matter.

A second interlaboratory project involved the sampling of the WAK reprocessing plant in Karlsruhe, Germany, by International Atomic Energy Agency (IAEA) personnel. Samples were shipped on resin beads both to ORNL and to the IAEA laboratory near Vienna; the latter also received dried samples to be processed in the conventional way. Both laboratories received dried material from which to load their own resin beads. Comparing the results in various ways gave good agreement, except for field-prepared spiked samples, where failure to attain isotopic equilibration between spike and sample rendered those analyses invalid. This problem can arise in any isotopic dilution technique and is not unique to the resin beads. Except for this case, agreement between field- and laboratory-prepared beads was excellent; agreement between IAEA and ORNL resin bead results was excellent; and agreement between all resin bead results and those obtained via conventional mass spectrometry was also excellent. We feel that this conclusively demonstrates the potential of the technique as a safeguard tool. One of the problems now facing us, as was demonstrated by our experience with the Japanese samples, is to ensure that our procedures are followed carefully enough to yield valid samples. Because the chemistry involved is straightforward, we are optimistic on this score, but it may be some time before the technique is adopted for routine use.

To further the acceptance of the resin bead technique, we are systematically trying to improve the precision routinely available with it. For example, in the past year, we have systematized the analytical protocol used on the mass spectrometers. Temperature, time, and count rate are carefully monitored to ensure that they remain within prescribed limits. A new ^{236}U spike is under evaluation; it should give a better measure of quantity, because it requires less bias correction with respect to the 238 mass position than does our old ^{233}U spike. Results of these efforts have thus far been encouraging with an apparent improvement in uncertainties from 0.8% to about 0.5%. There will be a strong effort in the coming year to effect further improvements in this area. (*R. L. Walker, D. H. Smith, J. A. Carter, T. R. Mueller*)

Minor isotope safeguards techniques. One of our major tasks this year was an analysis of 248 MIST (Minor Isotopes Safeguards Technique) uranium samples for a study of the Paducah diffusion plant cascade. The objective was to measure as precisely as possible the concentrations of the minor isotopes (^{234}U and ^{236}U). These, along with the ^{235}U/^{238}U ratio measured by Oak Ridge Gaseous Diffusion Plant (ORGDP), were to be the basis of an evaluation of the value of such measurements for use as a safeguards monitoring technique. Our three-stage mass spectrometer, with its high abundance sensitivity, is ideally suited for the measurement of minor isotope concentration; concentrations ranged from a few tenths of a percent to about 10 ppb.

Major changes in data processing have been made in an effort to improve results. In the new system, data for calculating the ^{235}U/^{238}U ratio will be collected first, and then the data for ^{234}U and ^{236}U will be collected in a second pass. We are hopeful that this scanning mode will lead to more precise measurement of ^{235}U/^{238}U ratios.

The cause of repeated problems with the preamplifiers in our ion-counting systems had to be investigated. The apparatus holding the divider network was redesigned to simplify multiplier installation. Electronic characteristics of the preamplifiers can now be investigated with our new diagnostic instruments. This allows us the capability to elucidate the cause of trouble as well as to set the various parameters correctly with a speed and certainty not previously possible. We feel confident that the weak link in our counting system has been substantially strengthened as a result of these studies. (*D. H. Smith, R. L. Walker, J. A. Carter, H. Simmons, L. K. Bertram, T. R. Mueller, E. G. Miller*)

Resonance Ion Spectroscopy Coupled with Mass Spectrometry

A joint investigation of the feasibility of combining resonance ion spectroscopy (RIS) and mass spectrometry was undertaken with members of the Health and Safety Research Division (T. Calcott, E. Arakawa, and D. Beekman) and J. P. Young of Analytical Chemistry Division. The idea was to use a tuned laser to selectively ionize a single element out of a mixture and to use the mass spectrometer to accomplish isotopic analysis. This technique, if perfected, would have significant analytical applications. A nitrogen-pumped dye laser was installed, and potassium was selected as the first element to be tested. We succeeded in making K^+ ions with the laser and in detecting both isotopes at the collector of the mass spectrometer, but various problems have prevented further progress. The laser collapsed and is now awaiting a specially ordered capacitor. The laser was pulsed in 10-ns bursts, and, unless we reduced its intensity, the number of ions generated in the short pulse far exceeded the resolution of our counting system. Our next experiment should use pulse-height electronic equipment to remove this difficulty. We hope to experiment on a system of greater analytical interest than metallic potassium; a mixture of rare earth elements is the likely choice. (*D. H. Smith, L. K. Bertram, R. J. Warmack*)

New gas mass spectrometer. The VG-Micromass MS 1201 gas mass spectrometer is now in use to analyze samples suited to its unique capabilities. It has been calibrated by use of several pertinent standard gas mixtures; a set of relative gas sensitivities is easily determined. The source and receiver ion beam defining slits are quickly adjusted to give the resolution of 2500 that is needed to separate CO and N_2, as well as C_2H_4 at mass 28. Analytical advantage is gained by the use of this procedure for separating ^3He and HD at mass 3, separating ^4He, HT, and D_2 at mass 4, and indicating N_2O next to CO_2 at mass 44. The peak-jumping feature (with the digital output recorded on a paper-tape printer) makes it very convenient to take background and sample data close together (in time) and in the same manner and greatly simplifies data reduction. Appropriate sets of peaks to be used in the analysis of various types of samples have been standardized. Satisfactory comparison checks with our General Electric gas mass spectrometer have been made with duplicate samples of ^{85}Kr, ^{133}Xe, H-D-T, and pure helium and argon cylinders. (*J. R. Sites, L. Guinn, M. M. Honaker*)

Mass spectrometry services. The Mass Spectrometry Service Laboratory continues to serve a wide variety of divisions and programs throughout ORNL, with about 60% of the analytical activities supported by the Chemical Technology and the Operations divisions. Preliminary, inventory, and returned separated stable isotope samples of 31 elements were analyzed. The resin bead technique has been extended to the isotopically enriched samples of ^{242}Pu from the present separation campaign. Purities of better than 99.9% are more easily determined than by the previously used solution sample loading method. Samples of americium, curium, and californium are now routinely submitted on resin beads for isotopic analysis. This process results in the handling and transferring of much smaller amounts of highly radioactive material and definitely stabilizes the mass spectrometer operation, thus yielding more reliable analyses. Quality assurance checks continue to use the standards of the NBS for uranium and plutonium on the Transuranium (TRU) mass spectrometer, isotopically normal samples on the solids mass spectrometers, and standard gas mixtures on the gas mass spectrometers. (*J. R. Sites, M. M. Honaker, L. Guinn, D. I. Whaley, R. L. Walker*)

ELEMENTAL AND ION PROBE SURFACE SPECTROSCOPY

Secondary Ion Mass Spectrometry

A digital link between a PDP-11/34 computer and the scaler output of IMMA was completed this year. Formerly, data, such as depth profiling and peak switching, were hand punched for reduction via an off-line computer. Now data are transferred directly to the PDP-11/34 for processing and storage. The digital plotter is also interfaced to the on-line computer. Programs have been written to receive data from the IMMA, process the data, plot the results, and recall any data stored earlier. An immediate increase in efficiency and accuracy was realized.

In many instances, secondary ion mass spectrometry (SIMS) allows one to perform mass and isotopic analysis on samples that are not amenable to other mass spectrometric techniques (e.g., surface ionization and electron impact). In our laboratory, we frequently encounter samples that are either radioactive, glasses, or refractory in unknown chemical form, or we receive samples that occur with some combination of these features. We have developed a method that allows the use of SIMS for the rapid, accurate determination of lithium and boron isotopic ratios in difficult sample types. The significant advantage for these samples that accrues from the use of SIMS is the complete elimination of any chemical preparation steps. The difficulties encountered in preparing these sample types for conventional mass spectrometric analysis has been treated in some detail in the American Society for Testing and Materials standards handbook.[5]

To demonstrate that the SIMS method provided the required accuracy in these isotopic determinations, it was necessary to show that no variable, and therefore uncorrectable isotopic fractionation, took place and that the unique, simple sample preparation method introduced no uncontrollable variabilities. The first application arose because, in certain instances, solutions of fissionable uranium are stored in vessels that are of unsafe configuration (from the standpoint of criticality). To ensure the nuclear safety of these containers, they are loaded with circular Raschig rings made of borosilicate glass. The ^{10}B in this glass has a large cross section for neutron adsorption, which reduces the nuclear reactivity of the stored solutions. These Raschig rings are sampled at regular time intervals and the $^{10}B/^{11}B$ ratio is determined to verify that no significant neutron-producing event has occurred.

In a second application, the method was applied to the analysis of aluminum oxide–boron carbide composite pellets. These materials are used in nuclear reactors as neutron shims (control rods) and usually contain from 1.5 to 4.0 wt % boron. Significant difficulty is encountered in preparing samples of this material suitable for conventional mass analysis because of the high aluminum content. It is not unusual to do the required sample chemistry and find that the final sample loaded into the mass spectrometer will not emit sufficient ion intensity to allow analysis. We have shown that the SIMS technique can be applied to these materials to provide rapid isotopic analysis of boron and any ^{7}Li that might be present as a result of ^{10}B neutron capture.

Another application of this method concerns the analysis of liquid solutions of unknown composition. Samples of this type are seen infrequently and are usually the result of an accident of some sort (e.g., Three Mile Island). Because of their unknown nature and the desire to establish their nuclear history, rapid analytical results are desired. The SIMS technique can be applied to samples of this type to provide both isotopic and quantitative information quickly.

In the analysis of borosilicate glasses, the first technique we examined was tailored to meet the SIMS requirement of a flat analysis surface. Small pieces, 0.5 to 1.0 cm, were prepared by crushing Raschig rings that had been used in uranium storage tanks and virgin rings that contained known normal boron. Several pieces of each sample were encapsulated into an epoxy resin and mechanically polished flat. The sample surface was presputtered to ensure removal of surface impurities and allow measurement of the "bulk" boron. We then used a 1-nA, ^{16}O^{-} primary beam to eliminate sample charging effects, and analytical data were acquired from a 50- by 40-μm region. Counting rates approaching 10^{5} counts/s were obtained for ^{11}B in the natural standard. Replicate analysis indicated that the sample exposed to fissionable uranium differed from the natural ^{11}B/^{10}B ratio (4.05) by no more than 0.045. In SIMS, one is always concerned about the possibility of hydride interference. We monitored the m/z 12 position and established that the hydride correction was no more than 0.28% of the ^{11}B signal. This initial experiment was very encouraging, because we were able to demonstrate that boron isotopics could be determined directly from the glass at 1% precision level with no cumbersome chemical preparation steps. The mechanical polishing of the samples is straightforward but is time consuming.

In the SIMS technique, it is recognized that some method of surface charge compensation must be employed in the analysis of insulator materials. This is most frequently achieved by using O^{-} primary ions because of the steady-state, self-biasing effect created by the emission of secondary electrons from the sample surface during primary ion bombardment. This effect allows a continuous, constant emission of sputtered secondary ions. When a true surface analysis of an unaltered insulator surface is required, O primary beams or some other form of surface charge compensation must be used. In this work we are concerned with overcoming the charging problems encountered with the insulator sample studied but are not constrained to perform a surface analysis. At this point we developed a simple sample-handling technique that eliminated sample charging as well as mechanical steps, such as encapsulation and polishing. This improved method was simply to grind the sample to micron particle size and distribute it as a very thin layer on a conducting substrate. In this mode the sample behaves like a conductor and no surface charge compensation is required; this allows the analysis to be achieved with whatever primary bombarding species is convenient.

We have gathered data, using electronic peak switching, on over 40 samples with this technique. When compared to a calibration standard, typical results show an accuracy of about 0.50% of the ^{11}B/^{10}B ratio for samples containing natural boron. These results have been obtained primarily from borosilicate glasses, but some results were obtained from nuclear grade aluminum oxide—boron carbide composite pellets. The method has been found to be equally applicable to either sample type. In the composite pellets, lithium isotopics also have been measured. The method has been applied to the analysis of boron and lithium in highly radioactive liquid samples obtained from the Three Mile Island reactor to provide both isotopic and quantitative information. In this instance the solutions were acidified, spiked with the desired elements, and a small fraction of a microliter loaded onto a conducting substrate. Because of the extreme sensitivity of SIMS, the radioactivity actually handled as a loaded sample was usually on the order of only 1 to 2 mR/h. In summary, the sample handling technique, in combination with the high sensitivity of the SIMS method, makes for a simple, reliable method for the rapid, accurate isotopic analysis of difficult sample types.

Considerable effort is being expended in the Solid State Division on the development of polycrystalline silicon as a matrix material for the production of direct solar/electrical conversion devices. We have provided significant assistance through our SIMS depth-profiling studies of boron in polycrystalline silicon.[6] This work has involved samples prepared by ion implantation (followed by laser and/or thermal annealing) and B_2O_3 high-temperature diffusion. We have developed a computer program for our on-line DEC PDP-11/34 to calculate normalized count sum areas from the observed concentration profiles. We have found that these areas were reproducible to within ±6% for a group of samples, including single and polycrystalline ion implantation standards, as well as for these same materials after laser annealing. Table 2.3 shows some typical integral boron data for a variety of samples.

Table 2.3. $^{11}B^-$ Integral count values (expressed as relative area)

Sample[a]	Date data taken	Relative area
TI as IMP-1	4-24	16.58
TI as IMP-2		10.80[b]
TI 0.88J-1		16.03
TI 0.88J-2	4-24	15.54
CVD as IMP	4-25	15.60
CVD as IMP+THER		14.65
CVD as IMP	4-27	14.01
CVD as IMP+THER		14.02
TI as IMP	4-30	16.44
TI 0.88J		16.69
TI 0.66J-1		15.47
TI 0.66J-2		16.50
	Average	15.6 ± 1.0
CVD + B_2O_3	4-26	7.03
TI + B_2O_3		2.49
MS + B_2O_3		1.64
SNG. XTL. + B_2O_3		2.44

[a] Explanation of symbols: *Type of polycrystalline silicon*—TI = Texas Instruments, MS = Monsanto, and CVD = chemical vapor deposition; *Treatment*—as IMP = ^{11}B ion implanted, J = laser annealed, THER = thermal annealed, and + B_2O_3 = thermally diffused.

[b] Example of bad data detection.

The reproducibility of the boron integral count area is such that it can be used to detect and allow deletion of bad data. This is illustrated in Table 2.3 at footnote *b*. The low value could be the result of the secondary mass spectrometer drifting off peak, but in any event the measured profile was in error and was discarded because of the low integral count value.

Workers in the Solid State Division have no way of knowing how much boron is taken up by a silicon sample during a thermal diffusion experiment. Our measured integral boron values are easily converted to total dose values. Furthermore, the observed profiles for the diffused materials are easily quantified (boron concentration vs depth) when compared with an implantation standard. Measurement of the integral boron count area has allowed us to use SIMS technique to show that no appreciable boron is volatilized out of the silicon substrate during the in-air surface melting phase of the laser annealing process.

In contrast to this work, we have studied the laser annealing in vacuum of ion implanted boron in silicon. In this study we were able to show, using quantitative depth profiling, that up to one-third of the implanted boron could be volatilized out of the silicon during surface melting when 15 successive laser pulses were used. Using 10 to 15 laser pulses produces a boron profile that approaches a rectangular distribution, which is a better shape for improved solar/electrical conversion devices.

The duoplasmatron ion source, used to generate the primary ion beam for IMMA, produces a very satisfactory yield of secondary positive ions for electropositive elements but has reduced sensitivity for most of the electronegative elements. A complementary method useful in producing negative secondaries is cesium ion bombardment. Cesium lowers the work function at the surface of the sample, and, since the availability of electrons is increased, a high yield of negative secondaries is expected, especially for the electronegative elements.

We have begun development of a cesium ion source designed to be interchangeable with the present duoplasmatron source on IMMA. One design, borrowed from G. D. Alton of the Physics Division, utilizes surface ionization of cesium vapor as it passes through a hot porous tungsten frit. Another type of source utilizes an indirectly heated tungsten frit loaded with a cesium-oxide-aluminosilicate material (dispenser cathode). The latter source proved to be very convenient to use, especially in evaluating changes in the ion extraction geometry. The new cesium ion source allows focused beams to less than 4-μm diam and standard operation of 2.5 nA into a 10-12-μm spot (2 to 3 mA/cm^2). A trajectory analysis performed on the cesium source geometry reveals that much of the beam is lost before it reaches the primary magnet. Work is under way to recover this loss by appropriate lensing that would thus improve the beam intensity.

Depth profiles were taken for arsenic and phosphorus implanted in silicon. For the arsenic samples, the normalized sensitivity was about a factor of 10 greater than when using the O_2^+ beam. In addition, interferences (from Si_2O) observed using the O_2^+ source were entirely absent using the Cs^+ source. Though the sensitivity for phosphorus was enhanced, its measurement was plagued by an SiH interference, which dominated the signal when using the O_2^+ source. Of course, the data can be corrected by use of the natural abundances of adjacent isotopes, although this results in an increase in noise.

We expect the cesium ion source to have unique applications for depth profiling of *n*-type implanted dopants in collaboration with, and in support of, the Solid State Division's solar cell development program. The spatial resolution will be useful in examining carbide formation in metals and in oxide films.

Workers in the ORNL Chemistry Division have shown that in situ formed oxides on Incoloy-800 tubes act as effective barriers to tritium permeation. To understand these barrier effects, characterization of the oxide coatings is necessary. To facilitate these studies, we have developed a quantitative SIMS technique that is applicable both to nickel- and to iron-based alloys. This method involves using a matrix ion species ratio to index an empirical sensitivity factor and has been described in some detail.[7] We have extended this method to the analysis of the above-mentioned films, with a significant improvement in analytical accuracy as compared to the single sensitivity factor method. It was earlier observed that the large changes in concentrations of elements in these oxides made the single-sensitivity-factor method inadequate for quantifying the observed peak intensities. Accordingly, suitable sensitivity-factor response curves were prepared by recording ion yields from an Incoloy-800 standard as O_2 pressure in the sputtering region was varied. During these experiments, the CrO^+/Cr^+ ratio was monitored for samples with high chromium concentration, and the FeO^+/Fe^+ ratio was used for samples that had low chromium concentration. Plots of sensitivity factors were made for Al, Si, Ti, Cr, Mn, and Ni relative to Fe ≡ 1, vs both the CrO^+/Cr^+ and FeO^+/Fe^+ ratios. Quantified depth profiles of the oxide films were then generated by noting the appropriate index ratio for each mass scan and using that ratio to select the correct set of sensitivity factors from the indexed sensitivity factor plots. These sensitivity factors were then applied to peak heights obtained from the mass scans, and elemental concentrations were calculated. It should be noted that "elemental" concentration in oxides refer to concentrations of metals in the oxidized states; in the bulk alloy, however, the metal components are truly elemental or alloyed. A detailed description of this study has been submitted for publication.[8]

Some of the more important conclusions drawn from this analytical study are given below. These findings apply to Incoloy-800 that was oxidized at 600°C under 0.94 atm steam pressure.

1. Pretreatment and surface cleaning techniques will change the material such that different oxides are formed.
2. Annealed materials tend to form thin oxides rich in chromium and manganese.
3. As-received materials that were lapped, buffed, and electropolished form thick iron oxide coatings.
4. Manganese, comprising about 1% of the bulk alloy, becomes dramatically enriched in the chromium-manganese type oxides, as much as 80% in some cases.

We have found that surface pretreatment affects oxide composition. As an outgrowth of this, a new direction in our program assesses the effect of laser annealing as a surface modification technique. The first two of a series of samples that were laser annealed prior to oxidation have been analyzed. Data were taken both inside and outside of the laser annealed area on each sample. On the least oxidized sample, a typical inhomogeneous oxide formed outside the laser annealed regions. Inside the laser annealed region, the film composition was quite different, being enriched in titanium and manganese in sharp contrast to the film outside the laser annealed region. A number of differences were observed in the more heavily oxidized sample between the laser annealed and the unannealed regions. The object of this investigation was to determine whether or not laser annealing will be a beneficial surface modification technique as it pertains to the tritium permeation behavior of the oxide films that subsequently form on such surfaces. (*W. H. Christie, R. E. Eby, W. J. Warmack, R. W. Stelzner*)

Surface Analysis

Quantitative ion implantation is finding increasing application as a method for preparing unique reference materials for instrumental analysis. The method is particularly useful in the preparation of surface analysis standards because ion implantation places the dopant species in the near surface region of a solid surface (typically from 100 to 2000 Å in depth). We have used standards prepared in this fashion to calibrate an SSMS for a near-surface region analysis of boron in an irradiated Zircaloy-2 fuel element cladding. The SSMS was the method of choice because of its demonstrated sensitivity and because our laboratory possessed an SSMS that was specifically designed to handle radioactive samples.

The object of this study was to determine whether or not significant boron had become permanently associated with the surface of Zircaloy-2 cladding samples that had been stored in an aqueous solution containing 5000 wt ppm of boron, isotopically enriched in ^{10}B. Consideration of the possible physical and chemical consequences of the type of exposure to boron that the samples had undergone led to the belief that the boron penetration was probably limited to 10 μm or less of the Zircaloy-2 surface.

The ability to deliver a precisely known dose in a known concentration profile makes ion implantation an excellent method for preparing surface analytical standards. The method is completely general in that any element can be implanted into a properly prepared surface of almost any material. Consequently, we prepared implantation standards at three different concentration levels using this approach. After implantation, these standards could be handled with little danger of altering the delivered dose.

The standards were prepared by implanting ^{11}B$^+$ in a polished Zircaloy-2 surface under high vacuum conditions (10^{-8} torr) at 100-keV implantation energy. The implant dose was measured to an accuracy of better than 5% by integrating the ion current delivered to the Zircaloy-2 targets. The projected range for 100-keV ^{11}B ions in pure zirconium (other components of Zircaloy-2 were ignored because of low abundance) is estimated from the Lindehard, Scharff, and Schiott theory[9] to be approximately 2000 Å, with a range straggling of 1080 Å. This would predict a broad implantation peak, as was evidenced by the depth profile data obtained through use of our ion microprobe mass analyzer. Data concerning these implantation standards are given in Table 2.4.

Table 2.4. ^{11}B implant standards

Standard	Implant dose (atoms cm^{-2})	μg cm^2	Peak concentration (at. %)
I	3×10^{16}	0.55	2.6
II	9×10^{15}	0.165	0.78
III	3×10^{15}	0.055	0.26

The three implant standards were subjected to IMMA analyses to verify the ^{11}B$^+$ implant dose levels. Data were recorded from a number of locations on each standard. The integral count values were used to calculate the ratios shown under the IMMA heading in Table 2.5. The ratios under the Theory heading were calculated from the measured ^{11}B dose delivered to each standard during ion implantation. The agreement is within the spread typically observed in secondary ion depth profiling studies.

Because the Zircaloy-2 samples were radioactive, small pieces for SSMS analyses were obtained by sawing with an Al_2O_3 cut-off wheel in a hot cell. A cold Zircaloy-2 blank specimen was cut as a monitor for both radioactivity and boron pickup. The specimens and blanks were then subjected to SSMS analysis. Group integrity was maintained so that the SSMS data for each sample and its blank, as well as an implant standard, were contained on a single photoplate.

The sparking technique used for analysis of the standards and sample specimens consisted of making a 0.03 nC exposure using a 25-μs pulse length at a 30-Hz repetition rate of 30-kV peak-to-peak spark voltage. This exposure was repeated at five locations on a specimen surface while integrating all transmitted ions at a single photoplate rack position to give a total exposure of 0.15 nC. A single 0.03-nC exposure

Table 2.5. ^{11}B in Zircaloy-2 implantation standards

^{11}B integral counts × 1000			Ratios		
Standard I	Standard II	Standard III	Standards	IMMA	Theory
1441	398.6	138.7	(I III)	10.9	10.0
1344	388.4	105.8			
1180	322.3	125.1	(II III)	3.0	3.0
1493	384.7	124.9			
1281	399.8		(I II)	3.5	3.3
1463	390.0				
1200					
Average 1343	380.6	123.6			

created a crater on the Zircaloy-2 surface that was generally 0.5 to 0.7 mm diam. The depth of this crater was visually estimated, by use of an optical microscope, as about 10% of the crater diameter. This technique was found to give easily readable ^{11}B lines on the photoplate for the 0.055 μg cm^{-2} implantation standard, and the crater depth was significantly deeper than the depth at which the ^{10}B surface contamination would be expected to occur in the irradiated samples. The five exposures consumed approximately 1.4 mm^2 of surface and, thus, should be a reasonably representative sample of the surface being analyzed.

The ratio of the intensities of $^{11}B^+/^{122}Sn^+$ was used as a calculation indexing technique for all of the Zircaloy-2 samples in this study. Tin is an alloying element in Zircaloy-2 and is usually present in the range 1.2 to 1.7 wt %. The isotope ^{122}Sn (isotopic abundance 4.8 at. %) produced photoplate line intensities suitable for ratioing to the ^{11}B line intensities in the implant standards. The average values of this ratio obtained for the three implant standards were used to construct a standard response curve. The curve was not a 45° line, because the response of the photographic plate is nonlinear for ion or photon detection when there are large variations in line exposures. It is for this reason that it was necessary to use an internal standard, such as ^{122}Sn, and ratio the blackening of the ^{11}B line to it, rather than to use the blackening of the ^{11}B line directly.

The $^{11}B^+/^{122}Sn^+$ ratio observed for the implantation standard in each sample group was used to construct a parallel response curve that should normalize out variations in plate sensitivity, sparking technique, and other variables related to the SSMS method. The $^{10}B^+/^{122}Sn^+$ ratios for all specimens recorded on that particular photoplate were converted to concentrations that use that particular response line.

In this study we have shown that ion implantation standards can be effectively used to calibrate an SSMS near surface analysis. Implantation standards can be made with accurately known doses of the desired dopant and are easily handled without fear of altering this [illegible]. Precise control of sample and standard sparking conditions in the SSMS provides the basis for calibrating an SSMS for near-surface region analytical studies. A detailed account of this investigation has been published.[10] (*W. H. Christie, R. J. Warmack, L. Landau, R. E. Eby, W. R. Musick*)

Instrumental developments for spark source mass spectrometer. In a typical SSMS analysis, the average standard deviation observed for an individual analysis is about 20%. Some of this uncertainty is due to variability in photoplate sensitivity and amounts to about 5%. The remaining error is usually ascribed to unreproducible spark parameters or to local inhomogeneities within the sample. Two instrumental developments have been made that show promise for reducing these imprecisions in spark source analyses.

A servocontroller was developed to maintain the spark gap width to a constant value. The gap width was recognized as an uncontrolled parameter leading to elemental discrimination effects in the observed mass spectrum. These effects were easy to observe in real time using the CEMA detector. An obvious improvement in analytical precision could therefore be realized by eliminating variances in the gap width.

The system detects the voltage developed across the gap before breakdown; this voltage, proportional to the gap width, is converted to a dc level and is conditioned to drive a voice coil actuator connected to the sample manipulator. This type of controller was first developed by C. W. Magee[11] at the University of Virginia for use with electrical detection on SSMS.

Operation of the controller showed not only that a constant gap width can be maintained but also that long exposures can be taken without operator intervention. Previously some samples, particularly low-volatility elements, such as iridium, required adjustment every few seconds to maintain the spark. The controller can easily control the spark for periods exceeding 1 h. In addition, graphite samples, which occasionally flake and short out the electrodes, are handled well by the controller. A second type of actuation is also being developed that uses a stepping motor instead of a voice coil. This would have application in controlling all three axes of the manipulator instead of just one.

Another device that is now being used in conjunction with the gap controller is a fast beam chopper. T. L. Futrell of the Y-12 Plant helped develop this device, which provides a reduction of sample inhomogeneous effects and a more controlled portion of the spark pulse to be recorded. In the asynchronous mode, the beam chopper allows random, small portions of the ion beam to be recorded on the photoplate. The duty cycle of the beam chopper can therefore vary the time required to obtain a specified exposure. Thus, more sample is consumed than is consumed without beam chop operation, and sample inhomogeneities are reduced. In the synchronous mode, the operator can additionally select a particular portion of the sparked ion pulse to be recorded. The more uncontrolled portions of the ion pulse, such as the initial and final portion, can be eliminated. This has been shown to provide as much as a factor of 2 improvement in precision.[12]

Both the gap controller and the beam chopper have been installed on one of our mass spectrometers and are in routine use. Results of analyses will be monitored over the next few months to compare the precision with the results obtained from the unaltered mass spectrometer.

Spark Source Mass Spectrometry for Highly Radioactive Materials

Under construction is a facility for the analysis of high-level γ-emitting samples. The facility will be capable of providing badly needed analyses for undiluted nuclear fuel processing solutions and solids. All the advantages of SSMS will be utilized, such as the capability for both elemental and isotopic analyses, the high sensitivity for virtually all elements, the solids analysis capability, and very simple chemical preparation of the samples.

The necessary steps preliminary to installation have been completed. First, a feasibility study[13] was undertaken that demonstrated effective remote operation of the mass spectrometer. The Engineering Division then designed the source shielding and sample transfer mechanism to interface the mass spectrometer to the hot cells in the High Radiation Level Analytical Laboratory of the Analytical Chemistry Division. A safety analysis document, which includes major features of the facility, a description of the operation, levels of radiation, typical sample sizes, and plans to handle special hazards, was written and approved. The surplus mass spectrometer to be used for the hot facility was procured, overhauled, and fine-tuned. The fabrication of source shielding and sample transfer mechanism is essentially completed, and installation is in progress.

The mass spectrometer has been modified for remote operation. Cabling has been extended to allow relocation of the control panel. Hydraulic operation of two valves has been changed to pneumatic actuation. The vacuum gages have been upgraded to provide more reliable operation. Prototype sample positioners have been assembled and are being evaluated.

When completed, the facility will handle samples up to about 100 R h^{-1} mg^{-1} at 1 cm. This will allow analysis of undiluted material without chemical preparation for nearly all reactor waste samples. Our low-level SSMS facility, which has been used to attempt analyses of very hot materials by dilution (to lower the radiation levels), will be returned to exclusive use for low-level samples. Essentially, the shielding factor of the new facility for ^{137}Cs gamma (0.66 MeV) is $\sim 10^5$ better than for the low-level facility. The high-level facility is expected to be completed and to be in hot operation during 1980. A summary report of our progress is published.[14] (*R. J. Warmack, D. L. Donohue, L. Landau, W. H. Christie, J. A. Carter*)

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3. Technical Support

L. T. Corbin, Section Head

The General Analytical Laboratory performed several important functions during the year. Thorium, uranium, ruthenium, and zirconium were determined for large numbers of differing sample types both by conventional spectrophotometry and by x-ray fluorescence in support of studies related to solvent extraction processes and solvent recycle. Many instruments were modified to serve current needs and to reduce maintenance costs. Wider application was made of ion chromatography to complement existing analytical capabilities. One laboratory was renovated and designated as the central repository for the University of Minnesota, Duluth, coal-gasifier samples. Another, the Environmental Analysis Laboratory, was moved to Building 1505. The sample-receiving room in Building 4500S serves as a clearinghouse for sample distribution throughout the Analytical Chemistry Division (ACD).

In the Radioactive Materials Analytical Laboratory, we continued to upgrade equipment, laboratories, and hot cells. The ORNL reactor fuel reprocessing programs required development of procedures for the determination of uranium, ^{3}H, and ^{14}C in dissolver solutions; of neptunium in tributylphosphate (TBP) solutions; and of the degradation products of TBP. New instrumentation included an automatic titrator, a density meter, a spectrophotometer, and a programmable pipet.

Work in the Transuranium Analysis Laboratory increased to more than 50,000 determinations. This 45% increase resulted from expanded experimentation in reactor fuel reprocessing.

The Reactor Programs Group began development activities in support of new reactor technology programs such as LWR Gel Sphere-Pac and Alternative High-Level Waste Forms. Development and evaluation of new or improved methods of analysis and instrumentation continued for the Consolidated Fuel Reprocessing and High-Temperature Gas-Cooled Reactor programs. Specific activities involved methods of analysis for chromium(VI), uranium, plutonium, urea, and hexamethylenetriamine. New instrumentation capabilities included thermal analysis, in-line gas chromatography, mercury porosimetry, and BET surface-area analysis. Another development effort was directed toward support of fuel reprocessing studies, which include engineering, process, and fabrication. Specific studies were sorption desorption of iodine on graphite, liquid chromatography for organophosphorus compounds used as extractants, and time-of-flight, mass-spectrometric on-line monitoring of effluents from fuel and waste preparation processes.

The Analytical Chemistry Division Data Management System (DMS) was expanded by the addition of three programs to provide for quality control, data transfer, and Gasifiers for Industry (GFI) program needs.

Our program for testing protective coatings has continued to grow. Special analyses were provided to the Three Mile Island Nuclear Plant and to Nuclear Fuel Services, Erwin, Tennessee.

DATA MANAGEMENT SYSTEM

The use of the DMS expanded during the year to six CD laboratories with either terminals or access to terminals. Four customer areas have their own terminals. Interest in the DMS from other laboratories continued, and the system has now been placed in a second location.

Several new programs were written this year to meet the growing needs of ORNL:

1. *Quality control* provides for terminal entry of quality control (QC) results, for detection of out-of-control situations by supervisors, and for access to the QC data and plots by the Quality Control Officer.
2. *Data transfer* provides for the transfer of completed results from the DMS to the customer's storage area, which eliminates the need for the customer to reenter his data before performing additional calculations.
3. The *GFI* program has been assigned a laboratory number to allow use of the DMS for documentation of sample receipt and transfer.

A graphics terminal has been obtained and will be programmed to display simulated distillation curves and calibration curves for spectrophotometric procedures.

Programming has begun on a format to meet the special needs of the GFI program. It will provide for an analysis catalog and the reporting of as many as 200 results for a single sample.

RADIOACTIVE MATERIALS ANALYTICAL LABORATORY

W. R. Laing, Group Leader

Upgrade of Hot-Cell Operations

Work continued in several areas of our plan to upgrade equipment for hot cells and glove boxes. The status of each item is as follows:

Automatic titration assembly. A Mettler titrator has been evaluated for both the Davies and Gray titration for uranium and the EDTA titration for thorium. The instrument was also checked for high and low levels of acid in the presence of large amounts of uranium, plutonium, and thorium. Complexing agents used were oxalate, fluoride, and iodate.

Parr density meter. A Parr density meter has been purchased, and plans were obtained from the Savannah River Laboratory to modify it for in-cell use.

Fiber optic spectrophotometer. Glass and quartz fiber optics were tested for radiation stability. Glass became completely opaque at 10^5 rd and was rejected from further consideration. Quartz showed little change in visible light transmission up to 10^9 rd. At this point the cladding of the fiber bundle deteriorated. Quartz fiber optics in the needed length (5 m) are not available at present. Work will continue when optics of a suitable length can be obtained.

Fiber optic fluorometer. Several problems delayed testing of the fluorometer on uranyl nitrate solutions. Incorrect filters were supplied by the manufacturer, and several designs of flow cells were required. The instrument is now ready for testing.

Programmable pipet. A Hamilton Microlab P pipet was tested and found to deliver aliquots with 0.5% precision over the syringe range. A problem was encountered in the "fill" mode in that, even at the slowest speed, the plunger was withdrawn so rapidly that air bubbles were introduced. A variable-speed controller was built, which lessened the problem but did not eliminate it. The precision was increased to 0.2% with the addition of the controller.

The Analytical Instrumentation Group continued to provide assistance in the development of an improved dielectric constant meter and in the work on a new in-cell pipet and titrator.

Building 2026 Maintenance

The item requiring the most maintenance in Building 2026 this year was the cell windows. Zinc bromide escaping through a faulty gasket penetrated the area behind the copper liner and caused extensive corrosion in one window. Working from the outside, the copper liner was removed, and the corroded area was cleaned. A mild steel liner was fabricated, installed in sections, and welded into place. A special gasket was made to seal against the inside lead glass. The outer glasses were reinstalled and the windows filled with $ZnBr_2$ solution. An inert cover gas was used to prevent corrosion of the mild steel liner.

A second window-maintenance problem was fogging of the surfaces of the 8-ton lead glass windows in the sample storage cell. The windows were removed and disassembled. Chemical cleaning proved ineffective, but the deposits were removed by polishing with cerium oxide. After a final cleaning with ethyl alcohol, the windows were reassembled, leak tested, and placed back in the storage cell wall.

Increasing friction in the intercell conveyor resulted in recurrent failures of the drive mechanism's slip-clutch. Recently we found that the rollers had frozen on several sections and that some sample bottles and a length of wire were caught in the tracks. After cleaning out the debris, the track was lubricated by use of a mixture of oil and kerosene applied with a pressure washer. At the same time the drive motor, gears, and clutch, all of which had been located in a recess behind lead brick, were moved to an adjacent recess behind a steel panel.

Other hot-cell maintenance work included replacement of storage-cell sample boxes, cleaning the inside window in cell 4, replacement of the in-cell balance, repair of the pipet, and decontamination and painting of cells 1 and 4.

Radioactive Materials Analysis

Sample load increased sharply during the year from an average of 1400 analyses per month in the first quarter to 2100 analyses per month in the fourth quarter. The increased number of analyses also meant increased analytical problems.

The inability to obtain high-precision uranium results on certain dissolver solutions was one source of concern. The presence of large amounts of nitrate and certain fission products was thought to cause the results to be erratic, even when the aliquot was cooked down and extracted into trioctylphosphine oxide. A spectrophotometric thiocyanate procedure was used as an interim measure until an ion exchange separation could be developed. The Reactor Projects Group found the best separation to be loading the uranium as sulfate on Dowex 1, eluting the fission products with washes of H_2SO_4 and HCl, and eluting the uranium with 0.05 *M* HCl. At about this time we learned that British workers were performing a direct titration on the dissolver solution by using an in-cell titration assembly for the Davies and Gray procedure. We fabricated a titration vessel, installed it in the cell, and have used it for the analysis of ten dissolver solutions to date. Differences of less than 1% were obtained between in-cell and out-of-cell titrations with use of this new assembly.

A variation of the ^3H distillation procedure improved the precision for samples high in heavy metals. The initial distillation was made from acid rather than from basic solution. For samples low in ^3H, the addition of base caused the formation of a large gelatinous precipitate, which had made distillation difficult. When the sample was left acid, the distillation was smooth. Because an additional distillation outside the hot cells was necessary anyway, the fission products distilled from the acid solution caused no problems.

The inability of engineers to obtain a ^{14}C balance across a fuel dissolver system led them to suspect the formation of organic ^{14}C-containing species. An apparatus modeled after the chemical oxygen demand apparatus used by water plants was built and evaluated. Silver-catalyzed dichromate was used to oxidize any organic materials. The evolved $^{14}CO_2$ was trapped in NaOH solution, reevolved outside the hot cell, and counted. Recoveries of ^{14}C from labeled organic compounds ranged from 85 to 100%. The apparatus has been used for spiked and unspiked dissolver solutions. Recoveries have been 85% in the hot cell, with sample results from 25 to 100 dpm/ml.

In studies of the photochemistry of the actinides, solutions of plutonium and neptunium in 30% TBP were submitted for neptunium measurement. Because a reliable method for stripping neptunium was not available, wet ashing followed by TTA extraction was used. The results showed poor precision and were complicated by the presence of plutonium on the counting plate. A method, based on an existing plutonium procedure, was used in which the sample aliquot was diluted with ethyl alcohol and then treated as an aqueous sample. Plutonium was reduced with hydroxylamine and ferrous iron, and the neptunium was extracted into TTA. Clean plates, free of plutonium, were obtained, and the precision of duplicate aliquots was 3%.

Ion chromatography has been used to measure the degradation products from organophosphorous extractants for nuclear reprocessing. In these studies, solutions were prepared containing degradation products from TBP, trihexyl phosphate, and tri(2-ethylhexyl) phosphate. Sensitivity of 10^{-6} *M* was found for dibutyl phosphate and 10^{-5} *M* for dihexyl phosphate. Di(2-ethylhexyl) phosphate eluted too slowly to have peaks of analytical value. Nine synthetic solutions containing 10^{-3} to 10^{-6} *M* dibutyl phosphate were prepared by Chemical Technology Division personnel for sample analysis. Results were within 10% of makeup in all cases. Further work on the application of ion chromatography to these problems is reported in the General Analytical Laboratory section.

Two special hot-cell projects were completed. Two samples of ^{241}Pu were separated from americium by ion exchange. The plutonium was adjusted to valence +4, absorbed on Biorad AGX4 ion exchange resin, eluted with dilute HNO_3-HF, and converted to the oxide. Four samples of plutonium with special isotopic content in a nickel metal matrix were dissolved and prepared for mass spectrometry. A cell was cleaned for this work, and new quartzware was used for the dissolution. Precautions were taken to prevent contamination from within the cell and cross contamination between samples.

Procedures have been established for the measurement of hydroxylamine and hydrazine in mixtures used as holding reductants for plutonium. Hydroxylamine was oxidized to nitrite with sulfanilic acid and iodine and was diazotized with 1-naphthylethylenediamine to form a colored species. This spectrophotometric procedure has a sensitivity of 1 μg of NH_2OH. Hydrazine was measured by a volumetric method in which it was oxidized to N_2 by a standard iodate solution in 6 *N* HCl. The hydroxylamine procedure is specific for NH_2OH, but the titration for hydrazine must be corrected for the NH_2OH present.

All Eppendorf-type pipets were tested for accuracy by pipetting a plutonium solution onto a plate and counting. Eight pipets, ranging in size from 20 to 100 μl, had biases of less than 1%. One 12-μl pipet had a negative bias of 1.7%.

Samples for analysis were received from the Three Mile Island (TMI) nuclear plant and distributed to other laboratories. No problems were encountered, and the work was completed rapidly in keeping with the need for this information. Help was provided to Chemical Technology Division engineers for the evaluation of ion exchange resins and inorganic absorbers for removal of radionuclides from the primary coolant water. Elastomers and pump seals that might be used at TMI were tested for radiation stability.

Testing of Coatings

The testing of paints, coatings, and other materials used in nuclear reactor primary containment areas has continued. Sample specimens, including coated-steel panels, concrete blocks, and other miscellaneous materials, were submitted by a total of 15 companies. Included among the more than 1300 test specimens were 23 systems for ease-of-decontamination testing, 910 specimens for radiation-resistance testing, and the remainder (including the irradiated specimens) for simulated loss-of-coolant-accident (LOCA) tests.

Decontamination tests are conducted in Building 3019. Irradiation testing is performed by use of the spent fuel assemblies at the High Flux Isotope Reactor (HFIR) fuel storage pool. The environmental test autoclave is located in Building 2026. *(R. F. Apple)*

GENERAL ANALYTICAL LABORATORY

R. P. Rickard, Group Leader

The General Analytical Laboratory (GAL) performed two important functions within the division. One was the management of a clearinghouse for analytical requests. This clearinghouse function involved the documentation of requests for technical support from both within and outside ORNL and the subsequent consignment of requests to appropriate groups within the Analytical Chemistry Division. Such a function will undoubtedly continue to increase in scope as other unique capabilities evolve. The principal function of the GAL, however, is to provide analytical support of a widely varied nature to programs within ORNL and, to a lesser extent, to honor requests for assistance from outside ORNL. Some of the more important analytical projects are reported here.

General Analyses

A large number of analyses were performed as a result of interest in reestablishing distribution coefficients for Th, U, Ru, and Zr between the extractant TBP-dodecane and simulated process streams. The distribution coefficients were known to be highly affected by the level of the degradation products, mono- and dibutylphosphate, in the extractant. To determine this effect under different solvent conditions required the analysis of both organic and aqueous solutions for elements of interest.

Another study was focused on means to rid the TBP-dodecane extractant of the degradation products to improve the solvent recycle capability. Techniques used employed complexing agents, such as hydrazine oxalate and hydrazine tartrate, which precluded direct use of conventional spectrophotometry for analyte measurements. We demonstrated that, by use of x-ray fluorescence, measurements for thorium, uranium, and zirconium could be made directly without interference from either the complexing agents or the degradation products.

Mono- and dibutylphosphate were determined in both organic and aqueous solutions. These phosphate compounds were stripped from organic samples with a weak solution of sodium hydroxide and were analyzed by ion chromatography. To determine the degradation products in carbonate solutions required the use of barium hydroxide as a precipitant for carbonate, followed by the use of a cation resin (Dowex 50W) to remove excess barium before making ion chromatographic measurements.

Samples of $Al_2O_3 \cdot B_4C$ and B_4C were analyzed for an outside agency by using ASTM methods to determine boron, carbon, and lithium. Single crystals of $M_2O_3 \cdot 11Al_2O_3$, where M = one or more alkali metals, were analyzed for K, Li, Rb, and Na content by using flame emission spectroscopy and atomic absorption spectrophotometry. The analysis was completed, however, only after overcoming difficulty in dissolving these inert crystals by use of low-temperature fusion of an ammonium bifluoride flux.

Studies to evaluate the utility of a proposed pyrochemical-dry processing method to reprocess spent reactor fuels required analyses for Th, U, Li, Cl, Bi, Al, and N. This process, involving simulated spent fuel, used molten lithium chloride as the fuel solvent, bismuth metal as a separatory phase, and ammonium chloraluminate as the actinide phase. In the process, the lanthanides remained in the lithium chloride while the actinides were transported through the bismuth phase into the ammonium chloraluminate. Analyses for the analytes mentioned were made in each phase material.

The following instrument modifications were made to accommodate new requirements or to correct recurring problems: (1) the ion chromatograph was equipped with a pulse dampener, in-line filters were installed, and larger eluent reservoirs were used; (2) the sintering furnace used for fluorometric uranium work was outfitted with sheathed lead-in wires, and the thermocouples were relocated to minimize maintenance; (3) a Leco sulfur determinator was equipped with a controllable vent on the downstream side of the combustion chamber to permit off-gassing of early combustion gases from leaf and vegetation samples; without this capability, an interference was encountered that seriously reduced the recovery of sulfur dioxide; (4) the Leco carbon determinator was equipped with a voltage amplifier, a voltage-to-frequency converter, a frequency counter, and a display to extend the analytical range from 2 μg of carbon to 1.5% levels, based on 100-mg samples. Recently a new Technicon Auto Analyzer II was acquired to replace an old analyzer system. Different cartridges were obtained, including blank ones, to provide more flexibility in the use of such an analyzer.

A laboratory has been established for the University of Minnesota, Duluth, coal-gasifier program. Sample receipt, preparation, distribution, and storage activities will be centered in this laboratory. Special equipment has been acquired to facilitate the handling of most of these activities according to ASTM guidelines, including a computer terminal for data-management purposes.

Environmental Analyses

The Environmental Analysis Laboratory was moved from Building 2024 to the new research laboratory in Building 1505. This was no small undertaking, since we had to maintain a high sample throughput during the time we were trying to correct certain malfunctioning facilities in the new laboratories.

Prior to analyzing large groups of samples, efforts were often expended to demonstrate the adequacy of sample-preparation methods. In anticipation of analyzing vegetation for arsenic content, National Bureau of Standards (NBS) orchard leaves were dissolved in a covered beaker by use of dilute nitric acid at an elevated temperature. The arsenic in the solution was determined by using the atomic-absorption–helium-glow-discharge method; complete recovery of the arsenic was indicated. Following this work, 75 samples of vegetation were ground to the consistency of orchard leaves, dissolved, and analyzed as above.

Arsenic was also determined in NBS fly-ash material by leaching with either 1 M or 6 M HNO_3 at an elevated temperature. The tests indicated that either of the two acid strengths was an effective leaching agent. Likewise, molybdenum was found to be leachable from fly ash with hot 1 M HNO_3, a procedure confirmed by comparing the analysis of the leachate solution with a solution obtained by completely dissolving the material. A leaching technique appears to obviate the need to completely dissolve fly ash for analysis of many of the trace elements.

The unique analytical capabilities of the Environmental Analytical Laboratory were used to analyze samples from outside agencies. High-purity quartz crystals from Oklahoma State University were analyzed to determine trace amounts of the alkali metals, iron, silver, and lead. We also provided the

Virginia Water Control Board and the Army Corp of Engineers with mercury analytical support. Silicon levels in calf-blood serum were determined for the Biology Division in support of an asbestos uptake study. The concentration of silicon in the serum was found to range from 1 to 6 μg/ml by using graphite furnace atomic absorption spectrophotometry. Numerous requests for mercury analyses continued to come from within ORNL. Principal requests involved stream- and river-water samples, sediments, and foods. Analytical parameters relating to sample volume reduction of water samples were studied to document the viability of this method. In this method general use is made of a dichromate-acid mixture ($HClO_4$–HC_3) as a stabilizing agent for mercury in water samples.[1]

TRANSURANIUM ANALYSIS LABORATORY

J. H. Cooper, Group Leader

The main effort of the Transuranium Analysis Laboratory was directed toward fuel reprocessing studies. Laboratory experiments in which plutonium, uranium, thorium, and nitric acid extraction coefficients were determined accounted for about 30% of our work. The stability of molybdenum and zirconium in simulated fuel solutions was studied, and many samples were submitted for the determination of Mo and Zr by colorimetric methods.

Hot-cell experiments using power reactor fuel contributed about 60% of our sample load. Many samples for uranium, plutonium, acid, nitrite, and fission product measurements were submitted from the solvent extraction program. Plutonium was determined radiometrically after separation by the thenoyltrifluoroacetone solvent extraction method. Plutonium in samples with no interferences was determined by gross alpha counting. After a precision and accuracy study, a colorimetric uranium analysis method was used when radiation levels permitted. In-cell dilutions of a uranium standard were made and analyzed by all analysts over a period of two weeks. The relative standard deviation was ±3%, with a negative bias of 2%. More than 100 determinations were made in this study.

To determine the stability of hydroxylamine nitrate (HAN) in nitric acid solutions, TRU operations personnel sampled solutions of HAN (0.5 to 0.9 *M*) and nitric acid (0.25 to 3.0 *M*) mixtures for several hours. Acid and HAN were determined by basic titration in 11 *M* LiCl with a recording servotitrator. Essentially no change occurred in the concentration of the components after 32 h. A similar study was made of samples that were air sparged for 7 h; again no change in HAN concentration was noted.

Samples prepared for isotopic analysis are no longer electroplated on wires. Instead, nanogram amounts of the actinides are adsorbed onto three to five ion exchange resin beads. The beads are separated from the sample solution and are submitted directly to the mass spectrometry laboratory. This method requires much less sample than did our previous method, and no prior separation is necessary.

During the Three Mile Island reactor crisis, Chemical Technology Division personnel requested gross beta-activity measurements on more than 700 samples they were using to ascertain the best ion exchanger for use in the cleanup efforts. Solutions representative of the waste water were spiked with cesium and strontium and passed through the ion exchange columns to measure the beta activity on the effluent samples. This was a short-term effort, but it required quick turnaround on results and around-the-clock coverage.

REACTOR PROGRAMS

D. A. Costanzo, Group Leader

Consolidated Fuel Reprocessing Program Studies

D. A. Costanzo is Program Manager for the division's "laboratory oriented" research and development work for the Consolidated Fuel Reprocessing Program (CFRP). Portions of the work are performed in (and reported elsewhere) other sections of the Analytical Chemistry Division. Here we report work for the CFRP that is carried out within the Technical Support Section.

Reference sample plan. A reference sample plan was issued.[2] The purpose of the plan was to provide a reference document that would facilitate coordination of research and development of methods, sampling systems, and in-line instrumentation in support of the Consolidated Fuel Reprocessing Program. The plan defines sampling locations, sample characteristics, and the sampling schedule needed to meet plant control and material accountability requirements for the proposed Hot Experimental Facility (HEF), a pilot-scale plant to demonstrate reprocessing technology for breeder reactor fuels. The plan also shows the current availability of applicable analytical methods and the status of research and development tasks on new techniques.

A second sample plan has been written and is in review. This plan was prepared in response to a new flow sheet adopted by the HEF. Modified Purex technology, which permits coprocessing of uranium and plutonium, will be applied; a new plan is needed to meet the requirements of the modified plant processing conditions and equipment. (*J. L. Marley*)

CFRP analytical support laboratory. An analytical laboratory was established in October 1978 in Building 7603 to provide technical support to Consolidate Fuel Recycle Program engineering development tasks. Photometric and titrimetric iron, free acid, nitrous acid, and NO_x measurements constitute most of the work performed. The number of analyses reported per month has been variable—from 67 the first month to 540 in July—with an average of 160 per month for 12 months of operation. (*J. L. Marley*)

Assay of plutonium. A potentiometric technique[3] was evaluated and adapted to the assay for plutonium in process solutions. For this method, a sample of fuel is dissolved by suitable techniques and thrice fumed with sulfuric acid. The material is taken just to dryness on the third fuming and redissolved in 0.25 *M* H_2SO_4. A weighed solution aliquot containing 20 to 30 mg of plutonium is taken, to which are added three 25-mg portions of solid AgO (added at 5-min intervals). Total oxidation time is 20 min, after which 3 ml of 1.5 *M* sulfamic acid are added to destroy the excess Ag(II). The solution is then made 3 *M* in H_2SO_4, and a slight excess of standard ferrous solution is added. The excess ferrous is then back-titrated with standard ceric sulfate. Recovery of plutonium is 100.04 ± 0.10% at the 25-mg level of plutonium. This work has been described.[4] (*C. S. MacDougall*)

Assay of uranium. The NBL-modified Davies-Gray titration method is known to be accurate, precise, and fairly specific for uranium.[5] However, erratic results have been observed upon analysis of high-burnup, fuel-process solutions for uranium. Radiolytic interference is believed to cause difficulties with the titration after TOPO extraction of uranium. To circumvent such problems, an anion exchange separation of uranium from fission products is being developed. In this technique, the uranium (in sulfate form) is loaded onto an anion exchange column packed with Dowex 1A-1X8 (50–100 mesh). Fission products and impurities are eluted by successive washes with 0.01 *M* H_2SO_4, 10 *M* HCl, and 6 *M* HCl, in that order. The uranium is then eluted with approximately 0.05 *M* HCl. This uranium eluate is fumed three times with H_2SO_4 and titrated potentiometrically. Tests gave recoveries of 99.65 ± 0.08% at the 50-mg level on uranium standards. Simulated high-burnup samples have been prepared by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ into samples of a synthetic fission product solution. These samples will be evaluated by the above anion exchange and titration procedure. (*C. S. MacDougall*)

Chromium(VI) analyses. Because Cr(VI) in 13 *M* HNO_3–0.05 *M* HF solutions accelerates the corrosion of stainless steel at the grain boundaries, a need exists for a method for determining Cr(VI) in the presence of CR(III) and other stainless steel cations in these acid solutions. The problem is to isolate Cr(VI). A ^{51}Cr tracer was used to evaluate ion exchange resins for the quantitative separation of Cr(VI) from these cations. We found that ion exchange resins tend to reduce Cr(VI) in acid solutions. Low cross-linked anion exchangers tend to reduce Cr(VI) more readily than higher cross-linked anion exchange resins, and high cross-linked cation exchange resins reduce Cr(VI) more readily than low cross-linked resins. Anion exchange resins reduced Cr(VI) much more readily than cation exchangers. The best ion exchanger found for the separation of Cr(VI) and Cr(III) was Dowex 50-1X, which had been pretreated with KOH—H_2O_2 solution and $K_2Cr_2O_7$ solution to oxidize the organic materials present in the exchanger. Standard methods are used for the determination of chromium. (*D. A. Lee*)

Liquid chromatographic separation studies. part of our continuing effort to characterize organophosphorus compounds of interest in nuclear fuel technology,[6-8] liquid chromatographic separation studies were carried out on mono- and dialkylphosphoric acids and also on selected neutral classes of trialkylphosphorus compounds, which act as extractants in nuclear fuel technology. For these high-pressure liquid chromatographic (HPLC) studies, we used a 25-cm Partisil-10 ODS-2 reverse-phase column, which employed methanol-water as the mobile phase. The mono- and dialkylphosphoric acids exhibit weak uv absorbance; however, we were able to greatly enhance uv detectability by preparing phenacyl and naphthacyl derivatives prior to injection onto the column. By tagging a molecule of interest with a strong uv chromophore, we were able to obtain liquid chromatography detection limits comparable to those of gas chromatography. The elution parameters for several mono- and dialkylphosphoric acids were evaluated. A report of this work has been published.[9]

Differential refractive index detection was used for the HPLC studies of neutral classes of organophosphorus compounds. Elution parameters were determined for substances that are representative of the trialkylphosphate, dialkylalkylphosphonate, and trialkylphosphine oxide class of compounds. A report of this work has been published.[10] (*D. L. Manning*)

A study of the nitric acid—sugar reaction. The disposal of high-level radioactive liquid waste is an important part of the nuclear fuel cycle. Waste solutions generated in the reprocessing of irradiated fuel are usually high in nitric acid. The practical disposal of this waste by proposed schemes (i.e., incorporation of the waste in glass—mineral-type cermet matrices—or storage as a liquid) requires the removal of the nitric acid. Hence, interest is renewed in the reaction of sugar with nitric acid as a means of nitric acid destruction and denitration. The objective of this project was to determine accurately the reaction rates of sucrose with concentrated nitric acid in the presence of low levels of iron, a corrosion product that has been reported to increase the rate and extent of reaction. The effect of temperature (100 to 110°C) and concentration of iron [0 to 0.2 *M* Fe(III)] on the basic nitric acid–sugar denitration was evaluated.

The following equations can be postulated for describing the overall denitration reaction:

$$12HNO_3 + C_{12}H_{22}O_{11} \rightarrow 12CO + 6N_2O_3 + 17H_2O \; . \quad (1)$$

$$12HNO_3 + 6NO \rightarrow 18NO_2 + 6H_2O \; . \quad (2)$$

$$24HNO_3 + 12CO \rightarrow 24NO_2 + 12CO_2 + 12H_2O \; . \quad (3)$$

From these reactions, it is inferred that 12 to 48 mol of HNO_3 will be consumed per mole of sucrose reacted. The overall efficiency would depend on the experimental parameters, not the least of which would be the initial concentration of HNO_3 and the rate of sugar addition. The rate of reaction at 100 to 110°C for an HNO_3 range of 6 to 9 *M* was found to be given by

$$-d(HNO_3)/dt = k[HNO_3][\text{sucrose}] \; . \quad (4)$$

Previous work by L. A. Bray at Hanford indicated that this relationship holds for acid concentrations as low as 1.5 *M*.[11] The acid-kill reaction, however, is very complex and, at HNO_3 concentrations above 9 *M*, does not appear to exhibit second-order kinetics, as had been previously assumed. Reaction rates as measured by the rate constant and efficiencies (moles acid destroyed per mole sugar) are in general higher when iron is present. Rate and efficiency of reaction decrease with an increase in temperature, as is consistent with an exothermic reaction.

The reaction products were monitored throughout the reaction. At high concentrations of HNO_3, NO was oxidized to NO_2. Therefore, an efficiency approaching 48 mol per mole sugar was observed, and copious quantities of NO_2 were evolved. However, as the overall reaction progressed and the concentration of HNO_3 dropped, the amount of NO_2 decreased as NO increased. This finding is consistent with the overall equations proposed earlier. The oxidation of sucrose is very complex, involving several hydrolyses, chain openings, and oxidation of alcohols to ketones and carboxylic acids. The final step is the severance of terminal carboxylic acids as CO_2. Thus, one does not expect great quantities of CO at any time and little is observed. At the higher concentrations of nitric acid, CO is oxidized to CO_2, which was observed. The overall efficiencies of 30 to 35 mol acid destroyed per mole sugar reacted are consistent with product formation. (*C. S. MacDougall*)

Determination of urea. A colorimetric method for the determination of urea by use of *p*-dimethylaminobenzaldehyde[12] was modified for urea determination in thoria–urania sols. Standard solutions were used to establish procedures to eliminate the interference of thorium, uranium, nitrate, and acid. Both thorium and uranium were removed from the sample solution before color development by precipitation as the hydroxides. An aliquot of the filtrate was then taken for color development. This aliquot was diluted to a predetermined volume, and its pH was adjusted to 1.0 with nitric acid. Small additions of solid $NaNO_3$ were made until a thin layer of $NaNO_3$ remained undissolved on the bottom of the containing vessel. This, in effect, adjusted the NO_3 concentration of all solutions (blank, standards, and samples) to a constant value. After overcoming these interferences, the precision of measurement for the molar absorbance of the colored urea-*p*-dimethaminobenzaldehyde reaction product was 3.4% over the range of 2.5 to 12.5 mg urea. (*F. L. Layton*)

Facility for spectrophotometry of radioactive samples. The hot-cell spectrophotometer facility, cell 7, Building 3019B, has been provided with absolute containment to permit measurement of solutions containing high levels of alpha, beta, or gamma radioactivity. This facility was originally designed by J. P. Young for the examination and study of radioactive samples from the Molten Salt Reactor.[13] Stainless steel panels were attached to the existing cell pan, walls, and intercell conveyor enclosure to isolate cell 7 from the rest of the cell bank and to provide the absolute containment. A Lexan panel was installed in the rear of the cell and provided with a removable entrance door, bag port, and glove ports for in-cell maintenance and waste removal. An enclosure was installed on the access drawer to cell 5 and is provided with a bag port and glove ports. A Cary 14H spectrophotometer with in-cell optics will be installed at cell 7 in the near future. (*J. S. Wike*)

High-Temperature Gas-Cooled Reactor Program Studies

We have continued to provide analytical development work and technical support for the High-Temperature Gas-Cooled Reactor (HTGR) Program. Significant projects are reported here.

BET surface area by inert gas absorption. A BET surface area analyzer, constructed by ORNL, was evaluated for the measurement of coal samples. A Cahn electrobalance is used to measure the sample changes in weight that are caused by absorption of an inert gas at isothermal conditions. The weight changes are then related to the surface area by use of a BET plot.[14] The sample pan suspension system of the balance was modified to reduce tare weight and bouyancy. These modifications resulted in an increase of 1 g in the load capacity and of 1 μg in the sensitivity of the balance. (*J. S. Wike*)

Thermal analysis. Thermal analysis equipment (DuPont 990 thermal analyzer) was purchased and made operational. The system includes a differential scanning calorimeter (DSC), a thermogravimetric analyzer (TGA), and a 1600°C differential thermal analyzer (DTA). Six Synroc preparations were evaluated by DSC and TGA analyses. (DTA analyses have been delayed because the 1600°C furnace burned out.) These materials include internal and external gelation preparations of mixtures of TiO_2, ZrO_2, Al_2O_3, CaO, and BaO to produce a rock-like material to immobilize high-level wastes for geological disposal. Five of the six preparations have very similar DSC and TGA thermograms. The other, a mixture of $CaCO_3$, $BaCO_3$, Al_2O_3, TiO_2, and ZrO_2, had thermograms distinctly different from the five gelation products. (*D. A. Lee*)

Graphite oxidation studies. In a joint effort with the Metals and Ceramics and the Chemical Technology division, laboratory experiments are under way to study the oxidation of reactor-grade graphites by moisture and the effect this oxidation has on the structural properties of the graphite. The oxidation studies are carried out in a closed-loop apparatus by use of helium as a carrier gas. The operating conditions of temperature, gas flow, and moisture in the helium sweep gas are varied to simulate the secondary coolant in an HTGR. Graphite species are to be characterized for density, surface area, and porosity before and after treatment.

Two corrosion apparatuses are used in the study. One is designed to accommodate brittle-ring specimens, and the other is designed for a range of solid cylindrical specimen sizes of various dimensions. Each is a closed system and contains a quartz reaction tube. Temperatures of the reaction zone are provided by a standard three-zone Lindberg model 54377 tube furnace. A gas circulating pump causes the moist helium to circulate through the corrosion zone. A copper water saturator to supply a constant amount of moisture to the closed loop was laboratory tested and found to provide moisturized helium at about 99% of the theoretical partial pressure of water over the range of the temperatures studied (0 to 20°C).

A Perkin-Elmer Sigma 1 gas chromatograph with an automatic gas sampling value has been installed on-line to monitor the corrosion products generated during the experiment. The gas analysis system has been calibrated to monitor the H_2, N_2, O_2, CO, CH_4, CO_2, and H_2O present in the system. The column contains Chromosorb 102 and is programmed to run from −40 to 175°C to effectively separate all the gases. By averaging values from five sample runs, precision and accuracy of better than 10% can be achieved for each gas. Gas concentrations in the range of 50 to 5000 ppm by volume were used for the precision and accuracy evaluations.

Before and after oxidation, the samples are measured for surface area, helium density, macroporosity (by use of a mercury porosimetry technique), and microporosity (by use of a modified BET technique).

An automated BET-type, surface-area apparatus was designed and built to measure the surface areas and helium densities of the samples.[15] Because of an unacceptable temperature rise in the gas manifold upon activation of any of the manifold solenoids, the apparatus had to be redesigned and rebuilt by use of pneumatic valves. A number of additional modifications were made to improve the flexibility and efficiency of the system. The gas manifold was constructed with 0.635-cm-OD copper tubing instead of the 0.318-cm-OD copper tubing that was used in the original design. The overall length of the manifold was shortened to keep the manifold volume the same (about 20 cm^3) in both designs. The system was designed to eliminate the need for the series of five calibrated volumes connected to the manifold. This design was accomplished by using the manifold as the calibrated volume and controlling the introduction of gas to, or the removal of gas from, the manifold by monitoring the pressure in the manifold as the gas was added or removed. The apparatus is now capable of measuring surface areas by adsorption or desorption; this capability was not available in the original design but is necessary for porosity measurements and for active site studies. The system is currently being interfaced to a Hewlett-Packard 9[illegible] desk-top computer for system control and data acquisition. The computer system will also be used to calculate the surface areas and to plot the isotherms on a Hewlett-Packard 9872A graphics plotter.

The macroporosity of the samples is measured by use of an Aminco mercury porosimeter, model 5-2171B. To improve its precision and accuracy, the porosimeter has been modified by the addition of three high-pressure Heise pressure gages. The precision and accuracy of the modified instrument have not been measured yet. (*J. D. Kintigh*)

Iodine sorption–desorption from graphite. We continued to work with the Chemical Technology Division in studies of the behavior of radionuclides in HTGRs. During this year we published two reports of work completed earlier on the transport of tritium and the distribution of fission products in the Peach Bottom HTGR[16,17] and began an experimental study of the sorption and desorption and iodine from H-451 graphite, which is the core material of the Peach Bottom reactor.

The overall goal of the iodine sorption studies is to evaluate the role of H-451 as an iodine sink during normal operation of an HTGR and as an iodine source under accident conditions. One objective of the laboratory studies is to measure the sorption isotherm of iodine on H-451 graphite at several temperatures and at expected operating conditions. Another objective is to determine the extent of desorption under conditions that simulate a coolant depressurization accident.

To meet these objectives, the uptake and release of iodine will be studied in two somewhat different experimental systems. In both systems, elemental iodine containing ^{131}I tracer in a low-temperature chamber (the saturator) is allowed to evaporate and saturate a helium stream that carries the gaseous iodine to a graphite specimen that is held at constant elevated temperature in a tube furnace. After leaving the saturator, the iodine is diluted with another helium stream before the gases enter the furnace tube. The iodine partial pressure to which the graphite specimen is exposed is thus controlled by the saturator temperature and the extent of dilution. The saturator is typically operated over the temperature range of −28 to −84°C, with a variation of about ±0.5°C at any chosen temperature. Graphite temperatures can be controlled over the range of about 250 to 1200°C, with variations of a few degrees. Helium flow rates are accurately controlled by throttle valves and are measured by linear mass flow meters. Except for the quartz furnace tube, all parts of both systems contacted by iodine are made of Pyrex. The buildup of iodine on the specimen is measured with a shielded NaI(Tl) gamma detector located under the tube furnace.

The first system, which has been in use for about four months, operates at a helium pressure of about 101 kPa (~1 atm). This system will be used primarly to derive sorption isotherms. To date, three experimental runs have been performed, with the graphite held at 428°C to yield a sorption isotherm over an iodine partial pressure range of 10^{-4} to 10^{-2} Pa (10^{-9} to 10^{-7} atm).

The second system will be operated at a helium pressure of about 1000 kPa (10 atm) and will differ from the first by having all glassware and quartzware enclosed in a pressure vessel. This system has been designed to equalize the helium pressure inside and outside the glassware and the quartzware within the pressure vessel.

After steady-state loading of iodine in the specimen has been attained (as evidenced by the gamma detector), the helium pressure within the pressure vessel and glassware will be rapidly lowered, and the amount of iodine released as a result of the depressurization will be determined. Currently, the pressure vessel for this system is being constructed. (*F. F. Dyer*)

Mass spectrometry. A time-of-flight mass spectrometer (TOFMS) has been used to monitor gaseous effluents from materials used in the HTGR Fuel Fabrication Program, the Light Water Reactor (LWR) Gel Sphere-Pac Program, and the Alternative High-Level Waste Forms Program in the Metals and Ceramics Division.

HTGR studies. The effect of CO_2 as a diluent in the pyrocarbon coating gas stream on the density and porosity of the inner low-temperature isotropic (LTI) carbon coating of HTGR fuel microspheres was studied by using the TOFMS to identify and measure the relative concentrations of the gases evolved. It was evident that CO_2 reacts with the coating gases

(C_2H_2 and C_3H_6) to produce H_2O and CO at 1200°C. Carbon surfaces were also eroded by the oxidation reaction: $C + CO_2 \xrightarrow[1200°C]{} 2CO\uparrow$.

Studies were made to determine the effect of the purge gas on the loss of carbon from (UO_3 + C) HTGR fuel microspheres. Purge gases used were Ar–4% H_2 and Ar–1% CO. In Ar–4% H_2, the loss of carbon was caused by CO evolution. The profile of the CO evolution curve and other significant mass profiles indicated chemical reactions occurring during the sintering process in Ar–4% H_2.

For the experiments in which Ar–1% CO was used as the purge gas, the loss of carbon was more difficult to detect because CO from the purge gas was in the sample continuously; however, an increased concentration of CO between 1400 and 1500°C was caused by the loss of carbon from the sample. At 460°C, CO_2 made a sharp appearance but subsequently decreased in CO concentration. This result was probably the reaction of O_2 (from UO_3 reaction) with CO to form CO_2. (*D. A. Lee*)

LWR studies. Calcination and sintering of urania gel fuel microspheres in Ar–4% H_2 and vacuum have been examined by using evolved gas analyses. Evolved gas analyses thermograms were made for all the significant masses found. A study of the profiles of the curves indicated the mechanism of decomposition and relative bond strengths of the components involved in the gelled microspheres.

Gas analyses were made on previously sintered urania gel fuel particles. Three sizes of particles (1000, 250, and 25 μm) were used for sphere-pac fuel for fast breeder reactors. The residual gases found in these microspheres were mainly CO and CO_2 (peak concentration 460°C). A broad peak of water was found between 200 and 500°C — peak at 360°C. Small amounts of fragments typical of aliphatic hydrocarbons were detected. The peaks in the thermograms for the 1000-μm particles were shifted to higher temperatures relative to the peaks for the smaller particles. This finding indicates that the residual gases are diffusion controlled from the interior of the particles.

A comparison was made between the pyrolysis of urania and that of thoria-urania gel microspheres. Ammonia was much more prevalent in urania than in thoria-urania spheres. The 385°C water peak from urania [dehydroxylation of $UO_2(OH)_2$] was very small for thoria-urania. Thoria-urania gels contain much more CO_2 than urania gels. Oxygen was released from urania gels when UO_3 was reduced to U_3O_8, but this reaction was not evident from thoria-urania gels.

An evaluation was made of $(Th\text{-}U)O_2$ gel microspheres prepared by the internal gelation process. The pyrolysis products from microspheres were monitored with the TOFMS at various programmed heating rates for NH_3, H_2O, CO, and CO_2. All data were stored on file in the PDP-11/40 computer and printed on an LA-36-DE DECwriter. The stored data were interfaced with several available Fortran programs. With program GRAPH, the computer produced graphs of peak heights of a mass to charge ratio (m/z) signal versus temperature. From the peak temperatures of these curves and the respective heating rates, Arrhenius plots were constructed and the activation energies were determined. They were 7.08 × 10^4 J/mol (16.9 kcal/mol) for NH_3, 7.33 × 10^4 J/mol (17.5 kcal/mol) for H_2O, 1.03 × 10^5 J/mol (24.7 kcal/mol) for CO, and 1.34 × 10^5 J/mol (32.0 kcal/mol) for CO_2.

The effect of three washing procedures on the removal of contaminants from $(Th\text{-}U)O_2$ gel microspheres was determined by pyrolysis mass spectrometry. The first washing procedure was a recirculation procedure starting with 1 *N* NH_4NO_3 and continuously diluting it with 0.3 *N* NH_4OH for 2 h. The second procedure was a "once-through" wash with 0.5 *N* NH_4OH for 1.5 h. The third procedure was a combination of the first two back-to-back for 3.5 h. Generally, wash 3 removed the most material. More nitrate was evident (NO^+, m/z = 30) in spheres washed with wash 1. Wash 2 removed the least amount of CO_2, possibly the result of the shortest washing time and the lack of salt to displace CO_2 before carbonato complexes were formed.

A comparison was made between $(Th\text{-}U)O_2$ gel microspheres exposed to the atmosphere and those not exposed. More CO_2 was released at 400°C for spheres exposed to the air than those not exposed. The release at 400°C indicates that stable inner-sphere carbonato complexes were formed; however, there was not a large difference between the amounts of CO_2 released from the two samples. More water than CO_2 was adsorbed from the atmosphere. (*D. A. Lee*)

Hexamethylenetetramine analyses. In the internal gelation process for the formation of HTGR fuel microspheres, hexamethylenetetramine (HMTA) has been used for the homogeneous precipitation of $UO_2(OH)_2 \cdot xH_2O \cdot yNH_3$, where $x = {\sim}1.33$ and $y = {\sim}0.67$. A nonaqueous potentiometric titration method was developed for the determination of HMTA. The solvent was acetonitrile, and the titrant was $HClO_4$ in acetonitrile. Excellent endpoints were observed by using platinum and antimony polarized electrodes. Urea did not titrate in this system, but NH_3 did.

Hexamethylenetetramine in acetone was titrated successfully with $AgNO_3$ in acetonitrile by using an amperometric endpoint. Wash solutions that contained NH_3, NH_4NO_3, urea, formaldehyde, and HMTA did not give an endpoint by this method.

The $2AgNO_3$·HMTA precipitated quantitatively from acetone solutions and could be weighed as such after drying at 110°C; however, NH_3, NH_4NO_3, urea, and formaldehyde interfered.

After the acid hydrolysis of HMTA to NH_3 and formaldehyde, formaldehyde was determined by the addition of an excess of standard KI-I_2 solution and was back-titrated with $AgNO_3$ by use of a specific iodide electrode.[18] We determined that the hydrolysis of HMTA was limited to about 97%.

The NH_3 from hydrolysis of HMTA may be determined by acid-base titration, using pH glass electrodes. An 8 *N* H_2SO_4 was used to hydrolyze HMTA, and the excess acid was back-titrated with standard NaOH to pH 5. Above pH 5, NH_3 and HCHO react to form HMTA. (*D. A. Lee*)

Leaching studies of synroc. Synroc, as the name implies, is a synthetic rock that is being investigated as a means of immobilizing high-level nuclear waste. The synthetic rock is formed from a mixture of oxides, principally TiO_2, BaO, ZrO_2, Al_2O_3, and CaO.

Leaching studies are being carried out on four samples of synroc that have been spiked with U-238 and varying amounts of one or more of the following isotopes: ^{239}Pu, ^{241}Am, and ^{244}Cm. Deionized water is being employed as the leachant. The leachings are being carried out at room temperature and atmospheric pressure for prearranged time periods. At the end of each time period, the leaching solution is analyzed by alpha spectrometry for the appropriate elements. The studies are scheduled to run for a period of six months. (*F. L. Layton*)

In another related study, synroc was prepared by external gelation for the purpose of incorporating high-level wastes as dilute solid solutions. Pyrolysis of this material from ambient to 600°C was monitored by the TOFMS. The NH_3, H_2O, CO, and CO_2 were the most significant products detected, and their thermograms were recorded. (*F. L. Layton, D. A. Lee, J. R. Kerrigan*[19])

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4. Bio-Organic Analysis Section

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The Bio-Organic Analysis section has continued to carry out and support environmental health research and is increasingly involved in disciplinary analytical chemical research and services. Activities focus on precise quantitative organic analysis and on the isolation and identification of organic constituents of complex mixtures. Bioassay chemistry, a term coined here to mean physicochemical aspects of biological testing, occupies much of our time. Inhalation bioassay remains a particular specialty.

The "Quantitative Group" is responsible for quantitative methods and services, especially in trace environmental analysis, petroleum substitutes, and polycyclic aromatic organic compounds. The "Qualitative Group" is engaged in chemical class fractionation, isolation and synthesis, and the spectroscopic identification of organic compounds. Our inhalation bioassay chemistry efforts, involving chemical, physical, and instrumental projects, are centered in the "Special Projects Group." Each group develops and applies new methods as required by section programs and by outside requests for assistance.

Our Life Sciences Synthetic Fuels Program and our Smoke Program each account for approximately one-third of our section support. The synfuels program is addressing the comparative chemical composition of petroleum substitutes, the identification of constituents responsible for their carcinogenic or mutagenic activity, and site-specific environmental and health assessments. The Smoke Program is providing results on the chemical characteristics of cigarette smokes, methods and instrumentation to determine dosimetry accompanying cigarette smoke inhalation, and methods for the generation and analysis of diesel fuel smokes for biological evaluation. The remaining support addresses research and special studies in environmental organic analytical chemistry. Problems in solid-waste disposal and in both particulate and vapor-phase organic air pollutant analyses are currently receiving attention.

Some of our most significant accomplishments are the identification of the alkaline mutagens in petroleum substitutes, improved quantitative methods through radiolabeled tracer studies, and an instrumental approach to monitoring dosimetry in cigarette smoke inhalation bioassays. A major upgrading of capabilities in infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and high-pressure liquid chromatography (HPLC) has also been achieved in this reporting period.

QUANTITATIVE METHODS AND APPLICATIONS

Unambiguous Determination of Benzo[*a*]pyrene in Petroleum Substitutes

The benzo[*a*]pyrene (BaP) content of a material is frequently determined as a measure of its polycyclic aromatic hydrocarbon (PAH) content. In the absence of biological data, BaP content is often used to estimate carcinogenicity, the primary indicator for giving priority to materials for carcinogenicity biotesting. The presence and quantity of BaP in synthetic crude oils and fuels is especially important because of the current concern about environmental and health effects accompanying any major U.S. synthetic fuels industry. Therefore, reports of "estimated" BaP concentrations and of new methods for the rapid instrumental determination of BaP have flourished. The reliability of the results and the methods are in question because assumptions are made about various steps in the procedures without validating them and because comparative data from other sources are not available.

We have addressed this issue by returning to first principles. A method was developed that determines the quantity of BaP recovered for analysis and identifies the material and its purity when it is isolated for quantitative measure. An abbreviated version of the conventional approach was developed simultaneously in the hope of providing a more practical method for routine use.

Both procedures are initiated by adding a carbon-14 labeled BaP [^{14}C-BaP] tracer to the sample. When viscous coal-liquids are analyzed by the conventional procedure, pentane-insoluble solids ("asphaltenes") are precipitated by adding pentane to a benzene solution of the sample. The supernatant is then subjected to (1) aqueous acid extraction, (2) aqueous base extraction, (3) dimethylsulfide (DMSO)/pentane partition, (4) DMSO/water/pentane backextraction, (5) Florisil column chromatography, and (6) acetylated cellulose column chromatography to isolate a BaP-bearing fraction. Samples are prepared in the abbreviated procedure by eluting a benzene or methylene chloride solution of the sample sequentially through Florisil, layered Florisil/alumina, and acetylated cellulose columns. The overall recovery of BaP is determined by liquid scintillation analysis of the isolate for ^{14}C content. Concentrations of BaP are measured by using gas chromatography (GC, BPhBT liquid-crystal column), direct-emission fluorescence (DEF), and HPLC [Zorbax octadecyl silane (ODS) column].

A low-Btu coal-gasifier tar, a coal-liquefaction product, a crude shale oil, a petroleum crude, and a diesel fuel prepared from shale oil were all studied by use of both procedures. These materials were chosen to provide data on important samples and to simultaneously challenge the procedures with materials of widely differing BaP content and physical properties. The conventional procedure, including final measurements by three methods, requires ten working days to process one sample in quadruplicate; six replicates may be analyzed in three working days by using the abbreviated procedure. We found that 60 to 80% of the BaP typically was recovered by the isolation procedures and that the abbreviated procedure yielded slightly lower recoveries than did the conventional procedure. Fluorescence spectra and the chromatograms resulting from gas or liquid chromatographic analysis are adequate to confirm the identity of the BaP.

Comparing the data in Table 4.1 by two-way analysis of variance showed that the difference between the results generated by the three measurement methods was not statistically significant (1% confidence level) to designate a given isolation procedure. Generally, results obtained by DEF agree better in comparing the two isolation procedures than did the GC or HPLC results. A statistically significant (1% confidence level) difference does exist between the results obtained by use of the two isolation methods, with the abbreviated method yielding results approximately 10% higher than the conventional method. This discrepancy is easily within the limits of certainty for the analysis of complex mixtures for trace levels of BaP.

Tracer recovery corrections, spectroscopic and chromatographic information on the isolates, and replication that uses the various procedures define the reliability of the results. Results that use more rapid methods may be compared with those reported here or with those generated by using these procedures. We are routinely employing the abbreviated procedure and two of the three analytical methods to determine the BaP content of a variety of petroleum substitutes. (*B. A. Tomkins, H. Kubota*)

Sampling and Analysis of Vapor-Phase Organic Compounds

Organic airborne pollutants distribute between the suspended particulate matter and the air to a degree that depends on their vapor pressures and on their affinity for the particulate matter. The vapor-phase constituents are typically collected on a solid

Table 4.1. Intercomparison of benzo[*a*]pyrene methods and results

	Procedure	n	BaP concentration[a] (μg/g), mean ± standard deviation DEF	GC	HPLC
Gasifier tar	Conventional	4	151.0 ± 2.7	148.0 ± 1.8	147.0 ± 4.7
	Abbreviated	6	153.0 ± 3.7	155.0 ± 5.0	164.0 ± 3.3
Coal liquid	Conventional	5	83.4 ± 2.6	81.5 ± 2.2	81.9 ± 6.2
	Abbreviated	4	86.8 ± 2.8	93.6 ± 2.4	95.0 ± 6.0
Shale oil	Conventional	4	25.9 ± 1.9	25.0 ± 0.8	24.8 ± 2.0
	Abbreviated	6	24.4 ± 1.7	27.4 ± 1.7	25.0 ± 1.7
Petroleum crude	Conventional	4	2.7 ± 0.18	2.2 ± 0.13	2.5 ± 0.23
	Abbreviated	6	2.4 ± 0.11	3.2 ± 0.32	2.6 ± 0.35
Diesel fuel from shale oil	Conventional	4	0.031 ± 0.005	*b*	0.028 ± 0.006
	Abbreviated	4	0.039 ± 0.001	*b*	0.050 ± 0.006

[a] n = number of replicate, DEF = direct-emission fluorescence spectroscopy, GC = gas chromatography, HPLC = high-pressure liquid chromatography.

[b] Concentrations too low to measure by gas chromatography.

adsorbent located downstream of a filter or on some other device designed to trap the particulate matter during sampling. The constituents of the vapor phase are determined in solvent- or thermal-extracts of the solid adsorbent. We are developing and evaluating methods for the quantitative determination of vapor-phase organics.

The first problem we addressed was that of replicate analysis. Most procedures in use require that the entire sampling cartridge be thermally desorbed or solvent extracted to provide a single sample for analysis. Important information can be overlooked or lost by such single analysis. We have examined the practicality of aliquotting the adsorbent to provide replicate samples from a given collection. We found that a 100-mg aliquot of a 3-g adsorbent trap is sufficient for thermal desorption GC analysis of the vapor-phase organics when sampling approximately 5 m^3 of air. Thus, we can perform 20 or more replicate or complementary analyses (e.g., with sulfur- and nitrogen-selective detection) on the contents of a single adsorbent trap and still extract a maximum amount of analytical information.

The second problem considered was quantitation. Because of the uncertainties in exactly reproducing instrumental conditions, sensitivity, and thermal desorption from week to week, an internal standard method of analysis was adopted. Careful examination of various vapor-phase samples led to the selection of 1,2,4-trichlorobenzene as the internal standard because of its elution in a clear "window" in the GC profile of the vapor-phase sample and because of its purity. This internal standard is added directly to the aliquot of adsorbent taken for analysis, and the solvent is flushed off with a stream of air immediately prior to thermal desorption.

Our current analytical procedure involves the thermal desorption at 250°C of aliquots of the sampling adsorbent, Tenax (most commonly Tenax −GC®, a 2,6-diphenyl-p-phenylene oxide polymer), directly onto the head of a glass capillary column held at −70°C in a GC. The column oven is temperature programmed to 160°C to elute the collected constituents, which are detected and measured by flame ionization. The internal standards method is employed in the computer-assisted calculations of the air concentration of each detected constituent.

Using our previously described[1] sampling system, we applied this procedure to samples collected by the U.S. Environmental Protection Agency (USEPA). The kinds of constituents that can be observed by use of this procedure are shown (Fig. 4.1) in the GC profile of a sample collected near a coal gasifier. The procedure in its current stage of development is capable of measuring at least 100 vapor-phase organics with boiling points in the approximate range of 40 to 250°C. These include paraffins from C[illegible] (peak 3) to about C[illegible] (not shown) and aromatics from benzene (peak 2) through 1-methylnaphthalene (peak 23). Difficult-to-separate isomers, such as the *o*-, *m*-, and *p*-xylenes (peaks 7-9), are resolved sample was concentrated on a precolumn and eluted directly onto an analytical column.

We have found it possible to fractionate crudely a petroleum substitute into aliphatic neutrals, aromatic neutrals, bases, and acids on a semipreparative scale aminosilane column (250 mm long, 10 mm ID) eluted with varying amounts of methylene chloride in hexane. This sample-preparation procedure offers several advantages over the traditional solvent extraction procedure, including a saving of time and a reduction in the amount of sample handling.

We have also concentrated PAHs in water samples by pumping a measured volume of the water across a small column (40 mm long, 4.6 mm ID) containing a reverse-phase LC packing. This column was then used as a precolumn in an analytical HPLC system (described below), which was designed to separate and determine PAHs. Tracer studies with ^{14}C-BaP indicate that better than 95% of the BaP is recovered from the aqueous sample by this technique.

Benzo[*a*]pyrene from various synfuel samples and a mixture of 16 PAH standards in water have been determined by HPLC. For the determination of BaP, isolates prepared from the various sources were eluted from a reverse-phase column (Zorbax BP-ODS; 250 mm long, 4.6 mm ID) with a methanol:water (93:7) solution. Absorbance of the eluant was monitored at both 254 and 365 nm. For quantitation of BaP, the absorbance at 365 nm proved to be very useful because BaP has a significant absorbance at this wavelength, but virtually all sample components that have chromatographic characteristics similar to BaP show negligible absorbance at 365 nm. Another advantage gained from monitoring at the two wavelengths is that the ratio of absorbance at 365 nm to absorbance at 254 nm (~0.55 for BaP) yields some indication of whether or not another component has been coeluted with the BaP.

For the routine determination of PAHs in water, the absorbance of the eluate was monitored at only one wavelength (254 nm). However, a fluorescence detector, capable of continuously variable emission and excitation wavelengths, was also employed in pilot studies. This dual detection system was advantageous because, of the 16 PAHs being determined (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]athracene, benzo[*g,h,i*]perylene, and indeno[1,2,3-*cd*]pyrene), three pairs were not sufficiently separated for accurate quantitative determination when isocratic elution from a reverse-phase column with an acetonitrile:water (70:30) solution was employed. Proper adjustment of the fluorescent excitation and emission wavelengths allowed a spectroscopic separation of these pairs (anthracene and fluorene, benzo[*a*]anthracene and chrysene, and benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene). In addition fluorescence detection is noticeably more sensitive for at least 8 of the 16 compounds.

It is clear that HPLC offers significant advantages over GC for quantitative analysis in many applications. We are taking steps to improve our HPLC capabilities. (*J. E. Caton*)

Introduction of Fourier Transform Infrared Spectroscopy Studies

A Fourier transform infrared spectrometer (FTIR) was acquired to expand organic structural identification capabilities of ORNL. The FTIR also expands quantitative analytical capabilities because (1) absorbances of 0.001 and less can be detected and accurately measured, (2) spectral subtraction can often successfully eliminate the absorbances of interfering substances, and (3) the baseline can be confidently adjusted to 100% transmittance. We have been applying FTIR to quantitative analytical problems ranging from analyses of gases in complex mixtures to studies of the interaction of PAHs with the surface of fly ash.

Using FTIR, gas samples have been analyzed for their content of NO, NO_2, CO, CO_2, COS, HCN, and SO_2. Sample types have included mixed gas standards, the gas phase of cigarette smoke, and the off-gas of a coal-conversion process stream. We find the FTIR easily capable of measuring absorbances of approximately 0.001 in these complex samples. Sensitivity is currently limited to about 250 ppm but can be improved 100-fold with the acquisition of a gas cell that has a longer pathlength. We believe that FTIR will find widespread application in the analysis of gas samples for several ORNL programs.

A second on-going application of FTIR has been for the surveillance of samples held in the USEPA DOE Synfuels Research Materials Repository. The intent is to note changes in the functional group composition of the samples accompanying long-term storage. In the process of routine screening, we have acquired data that confirm the potential utility of direct functional group determinations for assessing biological activity. A coal-liquefaction product and three hydrotreated versions (each differing in the degree of hydrotreatment) of the product were screened by FTIR. As the extent of hydrotreatment increased, the infrared spectra showed a decrease in the ratio of the absorbance attributed to amine and phenol functionalities to those attributed to the aliphatic stretching bands. This ratio was 0.12 for the starting product and 0.05, 0.02, and less than 0.001, respectively, for the low, medium, and highly hydrotreated products. Other work in the section has shown primary amino groups to be an important structural feature of alkaline mutagens in petroleum substitutes. Also we have determined that the mutagenicity of the oils decreases as the degree of hydrotreatment increases; therefore it may be possible to estimate the mutagenicity of such oils by direct quantitative analysis for functional group content by using FTIR.

The sensitivity and subtraction capabilities of the FTIR system were both thoroughly tested by a study of the transmission spectra of fly ash pressed into KBr pellets. The infrared spectra of organic compounds associated with the fly ash appear as perturbations in the baseline of the typical fly-ash spectrum, which shows major bands at 450, 800, 1100, and 3300 cm^{-1}. These major bands were isolated by subjecting the fly-ash spectrum to a very high degree of smoothing so that only the major bands remained. This smoothed spectrum is then subtracted from the original spectrum. By use of this procedure, preliminary studies of the different spectra have shown a good correlation between the intensity of the band arising from the aromatic C-H stretching vibration and the amount of BaP equilibrated with the fly ash. With this approach of subtraction of the smoothed spectrum, it may be possible to detect 0.05 ng of an organic compound on 3 mg of fly ash (10 ppb). This technique promises to find wide applicability to our work on the unambiguous quantitation of organics on fly ash, which is sponsored by the Electric Power Research Institute. (*J. E. Caton*)

Fossil Fuels Research Materials Facility

Research into the potential environmental and health effects of commercializing the production of petroleum substitutes requires evaluating many biological effects and determining the presence and quantities of many chemical constituents. The USEPA Health Effects Research Laboratory and the USDOE Office of Health and Environmental Research are encouraging the "matrix approach," whereby numerous investigators with different technical specialties examine the same set of samples as a means of increasing the rate at which useful information is generated. The success of this approach depends on the availability of suitable samples, which are best supplied through a central facility that is aware of current DOE technology priorities and of gaps in information on biological properties of important sample types. We have continued to fulfill this role of sample supplier and information-transfer agent. Associated analytical chemical research and services focus on generating reference data on the nature of the samples and on providing chemically defined materials, often chemical subfractions of the original sample, for study.

We have fulfilled an important practical need in this report period with the completion of physical facilities for storing research samples in quantities as large as 1 bbl (42 gal). The facility consists of two 2.4- by 12.2-m refrigerated cargo units capable of maintaining a total of 60 m^2 of storage space at 4°C. The units are mounted on a specially designed gravel bed to contain possible spills. A concrete pad located in front of, and extending between, the units is partially roofed to allow large-scale separation of material into aliquot for this to be performed outside the storage units. Each unit is fitted with explosion-proof interior lighting, self-contained refrigeration equipment, and temperature recorders to document storage conditions. Facilities have been upgraded by establishing a sample-handling laboratory to divide bulk samples further and by acquiring a word-processing system to maintain records and communicate experimental results.

An especially important collection of materials from the refining of crude shale oil has been processed by the repository during this reporting period. Approximately 15,890 m^3 (10^5 bbl) of crude shale oil produced at the Paraho Process Demonstration site were refined by the Standard Oil Company of Ohio into jet and diesel fuels. The repository obtained 200-liter quantities of the crude shale oil, intermediate process materials, and each refined product. These materials and their petroleum-derived equivalents were carefully, under quality control, separated into aliquot samples. These samples have been distributed to nearly 20 investigators, located across the country, for chemical and biological/environmental effects studies sponsored by the USEPA, the DOE, and the American Petroleum Institute. In addition, we have directed the attention of ORNL biological effects research groups to samples related to the H-coal process of liquefaction, to samples allowing the assessment of hydrotreatment effects on biological potency, and to more a detailed study of the Paraho SOHIO shale oil site. Carcinogenicity, mutagenicity, and acute toxicity are currently being examined.

We have initiated experimental efforts to document changes in chemical and physical properties of important sample types when stored for long periods of time. Viscosity, simulated distillation characteristics, infrared absorption spectra, and several individual constituents, such as BaP, phenols, and selected metals, are measured annually on the bulk samples. The study includes a comparison with aliquots that were stored under argon (in both flint and borosilicate glassware, protected from light) and with aliquots maintained at −20°C.

Our current inventory includes about 220 different sample types. Because it is impossible to thoroughly study so many samples and because many samples are available in limited (e.g., liter) quantities, we have selected a subgroup of samples for detailed study. These include Wilmington California crude oil, Recluse Wyoming crude oil, and a fuel oil blend from the Solvent Refined Coal process. These and the Paraho-derived crude shale oil samples are to be thoroughly characterized chemically and physically before they are distributed for biological research. It should then be possible to interrelate many chemical, physical, and biological endpoints and to return to the original sample supply for material to follow up important observations in the future. (*L. B. Yeatts, Jr., W. H. Griest*)

The Sorption of Polycyclic Aromatic Hydrocarbons on Fly Ash

The strong sorption[2] of polycyclic aromatic hydrocarbons (PAHs) on coal fly ash seriously hinders their quantitative analysis in this matrix. The sorption apparently is selective for aromatics and is inversely related to the PAH ring-system size. Five-ring PAHs, such as BaP, are difficult to extract from fly ash, and recoveries of less than 30% are common. Thus, analyses of PAHs, such as BaP in fly ash, can be biased low by factors of three or more, if corrections for extraction and isolation recoveries are not included. To develop more effective extraction procedures in the quantification of fly-ash PAHs, the nature of this strong sorption must be understood. We have begun studies to characterize quantitatively this sorption.

The first question addressed was the fate of the unextracted PAHs. Low-extraction recoveries can be caused either by incomplete extraction or by losses of extracted PAHs on glassware and other surfaces. We added a known activity of a ^{14}C-labeled BaP tracer (^{14}C-BaP) to a sample of fly ash and performed a solvent extraction. The tracer extracted in the solvent was measured by liquid scintillation spectrometry; that remaining on the fly ash also was measured by liquid scintillation spectrometry but after oxidation of the fly ash in a sample combustor.[3] We found that all of the unextracted BaP does remain with the fly ash, although this method does not indicate the speciation of extracted versus unextracted PAHs. When we examined spiked, but unextracted fly ash, we found evidence for a small but significant inhomogeneity in the distribution of the spike. Simple pipetting of tracer solutions onto the sample and evaporation of the solvent with stirring is therefore not an entirely satisfactory means of applying a tracer uniformly to a highly sorptive matrix.

The extent of the interaction between PAHs and fly ash is being probed by a frontal chromatography technique that we have developed. With this technique, a weighed amount of fly ash is dry-packed into a stainless steel column (250 mm long, 4.6 mm ID). The column is then equilibrated by pumping the appropriate solvent through it. After equilibration, a solution of a test ^{14}C-labeled PAH in the same solvent is pumped through the column until equilibrium (of the ^{14}C-activity pumped onto the column with that eluted from the column) is attained. The elution profile of the ^{14}C-activity reveals a considerable amount of information about the extent of interaction between the fly ash and the labeled compound. When this procedure was carried out with a benzene solution of ^{14}C-BaP, equilibrium between the tracer and the fly ash was attained very slowly. The equilibrium volume (150 ml) greatly exceeded the system void volume (4 ml) of the chromatographic system, indicating a significant sorption of the ^{14}C-BaP by the fly ash. In contrast, ^{14}C-dotriacontane in hexane rapidly equilibrated with the fly ash and showed an equilibrium volume that approximated the void volume of the system; this result indicated little or no sorption of this high-molecular-weight alkane by the fly ash. The sorption capacity of the fly ash for a given organic compound can be evaluated from the following expression:

$$Q = (D_f - D_0) \times C_0 \times V / D_f \times W\,,$$

where

V = the equilibrium volume (V_E) less the void volume (V_I). $V = V_E - V_I$ (ml).

D_T = the total amount of the ^{14}C activity pumped onto the fly ash to reach equilibrium [$D_T = C_A \times V$ (dpm)].

C_A = the ^{14}C activity in the eluting solution (dpm/ml).

D_O = the total amount of ^{14}C activity eluted from the column at equilibrium (dpm).

C_O = the concentration of the organic compound in the eluting solution (ng/ml).

W = the weight of the ash packed in the column (g).

Q = the capacity of the ash for the organic compound being tested (ng/g).

The sorption capacity of the electrostatic precipitator (ESP) ash was estimated by this technique to be about 25 ng of BaP per g of ash at 25°C in benzene. Such sorption capacity corresponds to a surface coverage of about 0.01% of the fly ash by the BaP. This finding suggests that very localized, highly active sites on the fly ash are responsible for PAH sorption.

Using this frontal chromatography technique and various perturbation treatments of the fly-ash surface, the components of fly ash responsible for PAH sorption are being probed. Both acid (0.01 *M* HCl in ethanol) and base (0.01 *M* NaOH in ethanol) pretreatment of fly ash tended to increase slightly its capacity to sorb BaP relative to untreated fly ash. Thus, Lewis acid and base sites on the ash do not appear to play a major role in PAH sorption. However, heating the ash for 16 h at temperatures of 200 and 300°C significantly increased the sorption of BaP. Heating for 16 h to temperatures in excess of 400°C essentially eliminated any affinity of fly ash for BaP. These results suggest a thermal uncovering/deblocking (200 to 300°C) of additional active sites, followed by a destruction or volatilization (~400°C) of the active moiety of the ash.

This approach is being continued with other treatments of the fly ash. Also, FTIR promises to allow an elucidation of the species involved in the sorption. An understanding of the nature of the PAH sorption will allow the development of improved methods of fly-ash extraction and also may shed light on the potential bioaccessibility of particulate PAHs. (*J. E. Caton, W. H. Griest, L. B. Yeatts, Jr.*)

ISOLATION AND IDENTIFICATION

Mutagenic Constituents of Synfuels

The industrial-scale production of petroleum substitutes may be accompanied by new environmental health impacts. An understanding of the constituents of the materials responsible for these observed biological effects is important in determining the nature of the problem and in suggesting remedial actions. We have made several important findings in the area of discerning mutagenic components of synfuels currently available from small pilot plants.

Potentially hazardous constituents of synfuels are found among several classes of compounds. Thus far, we have been concerned mostly with components of the basic and neutral fractions because short-term mutagenesis assays have consistently shown that these are the most mutagenic fractions. Certain basic subfractions have produced the highest *specific* (mutations produced/unit weight) mutagenic activities observed for any synfuel-related materials. The neutral fractions, while seldom having the highest specific activities, often produce the highest *overall* mutagenic activity because of the preponderance of these compounds (usually >50 wt %) in synfuel materials.

The basic fraction is defined in our fractionation scheme as the fraction of components that partitions in the ether phase of an aqueous (pH 11) ether solvent distribution system after removal of the neutral fraction in the preceding step. The ether-soluble base (ESB) fraction constitutes from 1 to 10 wt % of each of the synfuel materials that we have fractionated. Gas chromatographic mass spectral data have uniformly indicated that the basic components are all nitrogen-containing compounds. Simple pK_a calculations eliminate significant amounts of pyrrole-type compounds from inclusion in this fraction, leaving pyridine-type compounds and amines for consideration. Pyrrole homologues are distributed principally in the neutral fraction.

Subfractionation of the ESB can be accomplished in several ways. We have developed a particular subfractionation scheme, which is tailored to isolate the mutagenic components of the ESB. The scheme was developed without prior knowledge of chemical structures of the mutagenic compounds; it was achieved by applying a microbial mutagenesis assay to LC eluants divided into arbitrary volume cuts.

Experimentation with several chromatographic systems was required before a satisfactory isolation of mutagenic bases was obtained. A very good isolation of mutagenic activity (~90%) in about 10 wt % of the ESB was finally possible by use of a two-stage LC procedure. In the first stage, the ESB is eluted on a basic alumina column with benzene, followed by ethanol. Virtually all mutagenic activity occurs in the ethanol eluate. This eluate is next chromatographed on a Sephadex LH-20 gel column, which is eluted sequentially with isopropanol and acetone. The acetone subfraction is presumed to contain most of the mutagenic bases of the ESB, because about 90% of the ESB activity is accounted for in this subfraction. Application of this scheme to a number of different synfuel materials, as well as tobacco smoke condensates and a wood pyrolysate, has demonstrated consistent isolation of basic mutagens in the acetone subfraction.

Determination of the structural features of the nitrogen bases of the acetone subfraction offers a considerable challenge. Gas chromatography-mass spectrometry (GCMS) has been useful to the extent that this technique has confirmed the presence of nitrogen atoms (predominantly one per molecule) in each resolved component and has provided molecular weights for the major components. Because of the stability of the molecular ions, the apparent molecular weights observed, and the knowledge of the separation mechanisms of the two-stage chromatographic scheme, we conclude that the mutagenic bases are characterized by fused-ring systems incorporating one nitrogen atom within the molecule and having appreciable alkyl substitution.

Candidates for compounds of the type observed include nitrogen heterocyclics and amino-substituted PAHs. The GCMS techniques alone do not currently afford unequivocal differentiation between these two classes. Further examination has been carried out by employing chemical-derivatization methods. Acetone subfractions of coal-derived liquid and a shale oil were carried through a derivatization-reaction scheme with trifluoroacetylimidazole. Nitrogen heterocyclics are not derivatized, but primary and secondary amines are readily trifluoroacetylated at the active hydrogen sites. The products of the derivatization reactions were separated by solvent partitioning of the slightly polar derivatives into methylene chloride in contact with the aqueous reaction mixture. Results of these studies showed that the coal-derived acetone subfraction contains mostly amines and that the shale oil subfraction is composed nearly equally (on a weight basis) of aromatic amines and nitrogen heterocyclic compounds.

Current studies of the acetone subfraction are aimed toward identifying structural features of the major components. The expense of producing sizable amounts of acetone subfractions and the high degree of similarity in the physical and chemical properties of the compounds therein imposes many constraints on detailed elucidation of chemical structures. One avenue being pursued to confirm the mutagenic activities of the compound types implicated in these studies involves the synthesis of a few judiciously chosen compounds.

Mutagenic components of the neutral fractions of synfuel materials have not been studied to the same extent as have those of the basic fractions. Two classes of compounds included in the neutral fraction have been investigated to a limited degree: multialkylated PAHs and neutral nitrogen compounds. The separation of multialkylated PAH compounds and the subsequent determination of the contribution of this class to overall mutagenesis of the neutral fraction were carried out by Griest et al.[4]

Neutral nitrogen compounds, such as pyrroles, indoles, carbazoles, and benzocarbazoles, are a class that is referenced frequently in the chemical literature pertaining to synfuels. The importance of this class to the mutagenic properties of neutral fractions has not been established. In earlier studies of PAH subfractions, we determined that neutral nitrogen compounds are concentrated in PAH isolates. Percentage compositions have ranged from 1 to 10% of the PAH subfraction.

A separation procedure has been developed[5] for producing a neutral nitrogen-enriched subfraction. The whole neutral fraction is eluted from a Sephadex LH-20 column with isopropanol. Saturated compounds are separated in this manner (in the isopropanol eluate), whereas aromatic and neutral nitrogen compounds remain on the gel and are recovered by an acetone elution. The acetone subfraction is placed on a silicic acid column and eluted with a 1:3 benzene:hexane mixture, followed by a benzene:hexane mixture of 2:1. The last eluate contains the neutral nitrogen compounds. Performance of this scheme was followed using ^{14}C-labeled PAH and neutral nitrogen compounds.

Preliminary mutagenesis assays of these subfractions from a coal-derived liquid and a shale oil (same materials as discussed with respect to ESB fractions) show a modest amount of activity in the coal-derived subfraction, with no detectable activity in the shale oil subfraction. It appears that the contribution of neutral nitrogen compounds to the activity of a neutral fraction is small.

Figure 4.2 summarizes the status of our efforts to identify the constituents of synfuels responsible for their mutagenic activity. The separation paths to the active fractions are shown by the dark lines. To date, only the acid fraction has consistently shown the absence of mutagens. Mutagens in the alkaline fractions are characterized by polyaromaticity and high polarity. Neutral mutagens are characterized by polyaromaticity. (*B. R. Clark, C.-h. Ho, M. V. Buchanan*)

Studies on the Identification of Corrosive Agents in Coal Liquids

Unexpectedly high rates of corrosion [as much as 25 mm (1 in.) per year] have been encountered in some coal-conversion operations. We are currently collaborating with the Metals and Ceramics Division in an investigation of the causes of this corrosion. Our initial work is addressing corrosion problems observed at the Fort Lewis, Washington, and Wilsonville, Alabama, solvent refined coal (SRC-I) pilot plants. Samples of process-stream coal liquids collected from the fractionation towers at both plants, during operation under corrosive conditions, are being studied to scope the problem.

Little is known about the mechanism of the corrosion observed. Few measurements, either physical or chemical, have been made to compare the physical and chemical state of the coal-liquid with its corrosivity. Qualitative observations reported to date suggest only that several types of corrosion are occurring. Some effects seem to be clearly associated with flowing liquids, whereas others seem to stem from specific properties of liquid or vapor-phase constituents.

Preliminary investigations are focusing on physical and chemical properties of a few coal-liquids obtained from the plants experiencing the most corrosion. The liquids were moved from the feed stream to a fractionation tower at the Wilsonville plant and were sampled during high- and low-corrosion-rate situations. One feed liquid (produced in the conversion of a Kentucky coal) is particularly corrosive to the tower, whereas the other feed liquid (from an Indiana coal) is fractionated with considerably less tower corrosion. An obvious approach to relating chemical composition to corrosion phenomena is to examine compositional

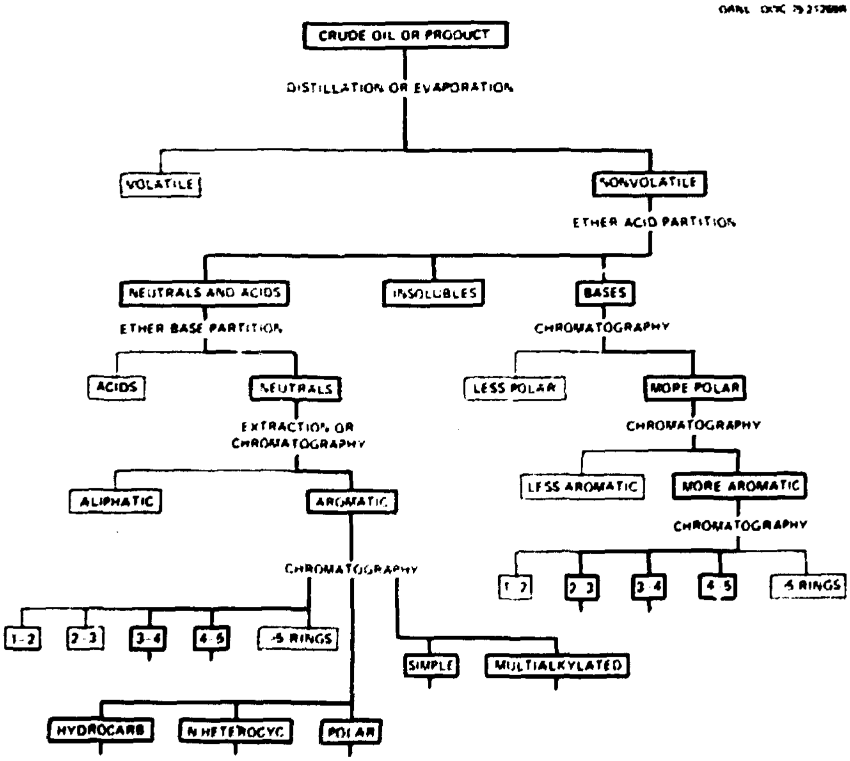

Fig. 4.2. Integrated chemical-biological approach to search for determinant mutagens.

differences between liquids that exhibit different corrosivities in the same process modules. The two Wilsonville feeds provide such an opportunity.

Sulfur and chlorine determinations revealed a tenfold greater amount of chlorine in the Kentucky feed (1024 ppm) than in the Indiana feed (116 ppm). Sulfur levels were 0.34% (Kentucky) and 0.23% (Indiana). The significance of the chlorine in these corrosion phenomena is not well established. Metallographic examination of the corroded surfaces did not show a corrosion typical of hydrochloric effects.

Definitive determination of the organic composition of the liquids is difficult because of the extreme complexity of these mixtures. However, certain comparisons can be made rather easily by using available methods. We separated each feed into neutral, alkaline, and acidic constituents by the use of the traditional ether-aqueous solvent partitioning. Neutral fractions constituted 90.4 and 91.3 wt % of the Indiana and Kentucky feeds, respectively. Basic fractions were 4.6 wt % (Kentucky) and 4.1 wt % (Indiana); the acid fractions were the smallest at 0.9 wt % for the Kentucky feed and 2.9 wt % for the Indiana feed. Small amounts of precipitates were recovered during separation of the acids. The GCMS analysis of the precipitates showed one major component: 2,6-di-tert-butyl-4-methylphenol. A negligible amount of insoluble bases was produced.

We subjected the whole, unfractionated feed liquids to direct GC and GCMS analyses; a polyimide glass capillary column was used. The most striking observation was that the GC profiles were qualitatively identical. When the chromatograms were overlaid, virtually all recognizable peaks had corresponding peaks in the other chromatogram. However, the relative amounts of the constituents (areas of the peaks) varied considerably. The Kentucky feed exhibited relatively greater amounts of compounds in the molecular weight range above methylnaphthalene. We found the major components of the Indiana feed to be tetralin, naphthalene, methylnaphthalenes, acenaphthalene (or biphenyl), and C_2-naphthalenes. We found that the Kentucky feed contained the same major components but, in addition, that it contained major quantities of other C_2-naphthalenes, C_3- and C_4-naphthalenes, acenaphthene, methylbiphenyls, anthracene-phenanthrene, methylphenanthrenes, fluoranthene, and pyrene. Few nonhydrocarbon compounds were found in either crude feed liquid.

We also analyzed the fractions by same method. Again, the GC profiles were qualitatively very similar. The components identified by mass spectral analysis were of the same classes as those we had observed previously in crude synfuel "ether-soluble base" fractions. These fractions include a broad spectrum of substituted pyridines, quinolines, and hydroquinolines in major amounts; alkyldiphenylamines and acridines in moderate amounts; and lesser amounts of carbazoles and benzcarbazoles. As expected, no hydrocarbons were observed in these fractions.

The acid fractions were also analyzed on the polyimide column, although this column is not ideal for the separation of free acids. Major components identified were phenols, cresols, and various, more highly substituted phenols. The Kentucky feed contains considerably more high-molecular-weight phenols than does the Indiana feed. No carboxylic acids were seen, although their presence cannot be excluded because they might not be eluted by the polyimide column.

Current and projected research into possible compositional features important to the corrosion problem is focused on the acid fraction. In addition, an effort will be made to determine the chemical state of dissolved, or precipitated, iron compounds that form in the corrosion process. Specimen coupons can be exposed to liquids in controlled environments operated by the Metals and Ceramics Division. Specific experiments are being planned jointly. (*B. R. Clark*)

Optimizing the Performance of the Nitrogen Selective Detector

The nitrogen-phosphorus detector (NPD) for GC provides the capability for selective detection of organonitrogen compounds. The NPD is similar to a flame ionization detector but is manufactured with a heated rubidium-silicate bead placed above the flame. Alkali ions cause enhancement of the detector current whenever nitrogen radicals are produced. The effectiveness of the NPD is a function of several operating variables: bead heating current, jet potential, carrier gas, air and hydrogen flow, and positioning of the bead. General situations for the use of the NPD have been presented in the literature, but, as has been suggested, each user should check the performance of each bead before applying it to his analysis.

We have used the NPD to detect organonitrogen compounds in a matrix of hydrocarbons. The optimum performance maximizes the nitrogen response and minimizes the hydrocarbon response.

Usually changes in one of the operating variables will cause both responses to move in the same direction, although not to the same degree. Hydrocarbon response can be reduced to zero, but this condition also produces a loss of nitrogen sensitivity, which may be unacceptable if levels are low. Most applications of the NPD appear to require compromise between sensitivity and discrimination. We have developed a useful approach for determining the parameter adjustments for optimum sensitivity and discrimination. A combination of factorial designs to evaluate the important variables and simplex designs to reach the optimum response provides a statistically sophisticated, yet-simple and quick, solution to the optimization problem.

The experiments to develop the optimization scheme were performed with instrumentation that is used routinely for organonitrogen analyses. Settings similar to those recommended in the manufacturer's instructions were used initially. The bead location was set as instructed and was not changed for this study. However, the bead location is a parameter that does affect the sensitivity and discrimination but that is not easily quantified. The parameters considered for these studies were: bead heating current, detector air pressure, and detector hydrogen pressure. Benzene solutions of carbazole and octadecane were used as representative organonitrogen and hydrocarbon compounds. Twelve component mixtures of each of these classes were used to demonstrate discrimination between compound types.

Two factorial design experiments were used to define both the region in which the optimum discrimination factor (ratio of carbazole to octadecane responses) was favored and the important experimental variables. Results of the first factorial experiment indicated that the discrimination factor was improved by using lower air and hydrogen pressures and higher bead heating-current levels. Only eight sets (bead heater setting, H_2 pressure, and air pressure) of data points were required for this first experiment. A second factorial experiment was designed and conducted with a smaller range of levels for the variables.

The factorial experiments indicated the area in which the optimum pressures and bead current settings should be found (i.e., hydrogen pressure, 8 to 10 psig; air pressure, 18 to 20 psig; bead heating-current setting, 650 to 660). A more precise determination of optimum operating conditions was obtained by a simplex experiment to maximize the ratio of the carbazole response to the octadecane response. In the generation of data from ten variable settings (vertices), one vertex was chosen as the maximum optimum set of conditions: bead current, 660; air pressure, 20 psig; and hydrogen pressure, 6 psig. The hydrogen pressure boundary had arbitrarily been set at 6 psig because it was feared flow control might not easily be maintained at lower pressures.

There is contradictory evidence about the stability of the detector bead. In the course of these studies, there was a noticeable decrease in detector response; sometimes, there were short-term aberrations that corrected themselves. Consequently, it is necessary to run periodic performance checks; if reoptimization is required, a short simplex series can be carried out. Response varies with the type of nitrogen-containing compound and is not correlated with the number of nitrogen atoms in a molecule. Therefore, if one is investigating a specific compound or class of compounds, it would be better to use that compound for the simplex experiments.

Our work has shown that statistically organized designs are useful for determining the optimum parameter settings for the NPD when it is being used to discriminate between hydrocarbon and nitrogenous compounds. A combination of factorial and simplex experiments proved to be effective in this study. This type of procedure is applicable to other detector-response situations in which there are several variables. The statistical method provides a rapid and efficient means for finding optimum operating conditions and permits an analysis of the effects of all the variables and their interactions.[6] (*I. B. Rubin, C. K. Bayne*[7])

Introduction of Nuclear Magnetic Resonance Studies

Nuclear magnetic resonance (NMR) spectrometry has been added to the capabilities of the Analytical Chemistry Division. This capability is finding immediate applicability in surveying the nature of chemical subfractions of synthetic fuels and in general organic structural identifications work. This report introduces the new capability through a description of the newly acquired instrumentation and its application to identifying the structure of dyes and impurities in the dye formulations for the Department of Defense.

In late August of this year, a JEOL FX90Q Fourier transform NMR spectrometer was installed as part of our structural identifications facility. This instrument can routinely obtain spectra with 10-, 5-, or 1.7-mm (micro) sample tubes on a sample as small as a few micrograms. A multinuclear probe has recently been ordered, which will allow all active nuclei between 6.5 and 90 MHz (at 21.5 kG) to be observed. These include ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{31}P, and ^{29}Si.

The FX90Q has a highly flexible software package that includes simultaneous data acquisition and reduction. Stacking of commands so that the NMR spectrometer can work unattended to obtain information on a series of experiments on one sample is also possible. This method allows overnight and weekend use of the instrument for long-term experiments, such as T_1 measurements on microsamples, and thereby avoids monopolizing the instrument for routine use during normal working hours. The capabilities of the instrument include not only coupled data acquisition, but also homonuclear and heteronuclear decoupled data acquisition. Measurements can also be made of nuclear Overhauser effect, off-resonance decoupling, spin-lattice relaxation and other standard NMR experimental techniques. One of the initial uses of the instrument has been the analysis of a series of four-colored smoke dyes used by the Department of Defense. The four dyes, red, violet, green, and yellow, are all derivatives of anthraquinone. The proton NMR spectra of the dyes all have non-first-order spectra in the aromatic region between six and eight parts per million and, thus, give very little insight into the molecular structure. Therefore, ^{13}C NMR was used in the structural analysis. The proton decoupled ^{13}C-NMR spectrum of the impure "red" dye was obtained on a 5% solution in chloroform-d_1, by using a 18°-pulse angle and a 10-s pulse interval. There were 15 resonance peaks in the major component of the dye, methylaminoanthraquinone, including two carbonyl carbons and one carbon belonging to a *n*-methylamino substituent. A NOE, proton coupled spectrum of the impure dye allowed the distinction between the protonated and non-protonated carbons. We were able to assign all 15 carbon resonances to the various carbon atoms in the molecule. The ^{13}C NMR spectrum of 1-methylaminoanthraquinone obtained commercially was identical to that of the red dye. Impurities in the red dye were not seen in the ^{13}C NMR spectra because of their low concentration.

A 2% solution in dimethylsulfoxide-d_6 of the "violet" dye, composed mainly of diaminodihydroanthraquinone and methylaminoanthraquinone, was used to obtain ^{13}C NMR spectra with an 18°-pulse angle and a 10-s pulse delay. The proton decoupled spectrum showed seven resonance lines, one of which was indicative of a carbonyl carbon. The NOE proton decoupled spectrum aided in the assignment of these resonance lines to the seven pairs of magnetically equivalent carbon atoms present in diaminodihydroanthraquinone. A commercially obtained sample of this compound yielded an identical ^{13}C NMR spectrum.

The methylaminoanthraquinone was not observed in the ^{13}C NMR spectrum of the violet dye. However, direct probe mass spectrometric analysis showed that the compound, diaminoanthraquinone, and at least two other minor components are in the impure violet dye formulation. The same experiment was done on the impure red dye, and at least three components were tentatively identified: methylaminoanthraquinone, anthraquinone, and azobenzene.

To separate the dyes for structural identification of the impurities, semipreparative LC was used. For the red dye, a 10-mm-OD by 250-mm-long Lichrosorb C_{18} (5-μ particle size) reverse-phase column was used with a 50:50 mixture of acetonitrile and water. Approximately 6 mg of the dye in 100 μl of methylene chloride was injected, and six peaks were collected, including one purple eluate and one orange eluate. The chromatographically separated fractions were then freeze-dried to remove the solvent and transferred to a 1.7-mm-NMR sample tube for study by both ^{1}H and ^{13}C NMR. The materials are being analyzed to determine their identities, and methods are being developed to prepare sufficient quantities for biological testing. (*M. V. Buchanan, I. B. Rubin*)

SPECIAL PROJECTS

Instrumental Dosimeter for Large-Animal Smoke-Inhalation Exposures

Dogs are favored by many experimental toxicologists for studies of inhalation hazards. Dogs are commonly used in tobacco smoke studies to evaluate biochemical, respiratory physiological, and oncogenic impacts. The standard technique requires that a machine generate and deliver a metered volume of smoke to a stand tube. The contents of the tube are then involuntarily inhaled by the dog through a tube (cannula) that is inserted in the dog's trachea. Cuffed cannulae, intratracheal tubes fitted with what amounts to a balloon above the delivery orifice, isolate the upper respiratory tract from the entering smoke and eliminate the possibility of smoke or air being inhaled or exhaled through the dog's mouth or nose. Only inhaled and exhaled air (periodically containing a puff of cigarette smoke) is available and is exhausted only through the cannula and connected stand tube.

We believed that this configuration would ensure inhalation of all of the insulting agent (in this case, tobacco smoke) provided by the machine and, thus, result in a complete, reproducible, and easily quantifiable dose of the test agent to each animal. This result has not proved to be the case. Instead, the quantity of smoke provided to the animal is dependent on the peculiarity of the smoking machine, and the fraction of the provided smoke that the animal will ultimately inhale or retain depends on the individual respiratory characteristics of that animal. Thus, the amount of smoke that is actually inhaled differs greatly from that which may have been expected and varies from day to day and from animal to animal.

Given the impossibility to control dosimetry, it is crucial that whatever dose is achieved be quantitatively monitored. We have developed an instrumental system that promises to achieve this quantitative monitoring, which is based on simultaneously measuring air flow rates and smoke particle concentrations and combining the outputs to provide a continuous measurement of inhaled smoke.

The instrumental configuration is depicted in Fig. 4.3. The dosimeter works on the principle that the product of the smoke concentration that enters the animal's cannula and the instantaneous flow rate at which it enters, integrated over the period in which the animal is exposed, is equivalent to the smoke dose that the animal inhales. Smoke particulate concentrations are determined with a combination light-emitting diode-phototransistor device. The operation of the device, its response to a wide range of smoke particulate concentrations, and the supporting circuitry have been described.[8] Briefly, the sensor measures instantaneous smoke concentration at the entrance to the tracheal cannula by monitoring light that is backscattered from the smoke particulates. Inhaled-air flow rates are measured with an 80 liter/min pneumotachograph inserted in the inhalation valve of the animal's exposure system. (A pneumotachograph is a laminar flow device, which is used by physiologists to measure human respiratory function.) Because the pressure drop through the pneumotach is so low, it does not interfere in any way

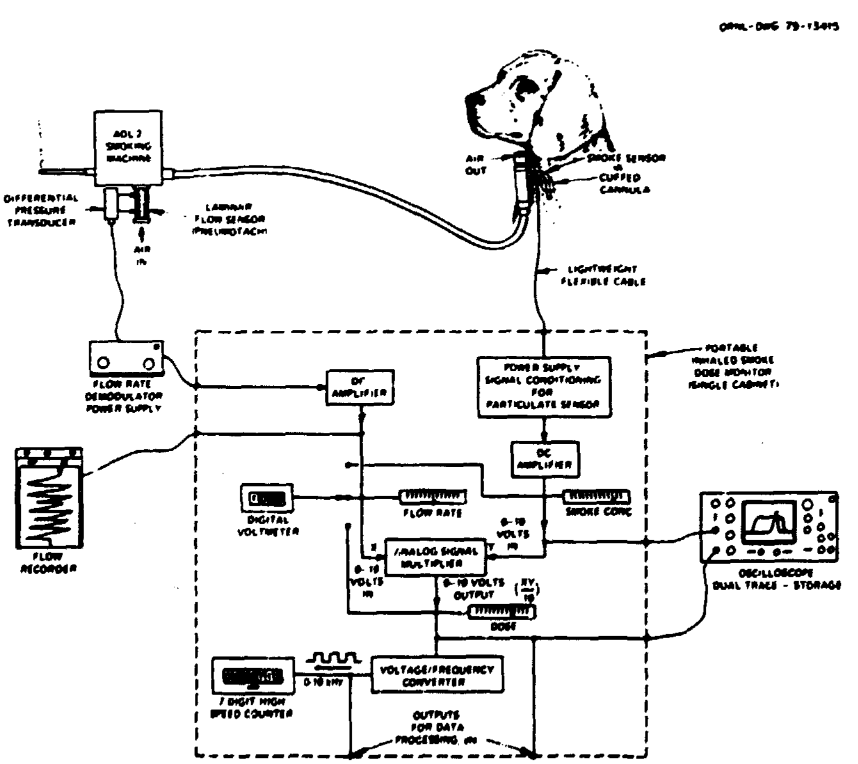

Fig. 4.3. Schematic diagram of instrumental inhaled-smoke dosimeter.

with the animal's breathing. Extensive testing verified that flow rates measured at this point in the exposure system were essentially identical with those that were actually occurring in the tracheal cannula.

Details of the instrumental dosimeter's configuration and supporting circuitry have been presented elsewhere.[9] Briefly, a demodulated signal from the pressure transducer-pneumotach is amplified and multiplied by the amplified smoke-concentration signal. The resulting product is integrated with a voltage-to-frequency, converter-based, ORNL-designed, digital integrator. The resulting output, in counts per cigarette, is related directly to the amount of smoke particulates passing by the sensor, regardless of the particulate velocity.

The performance of the inhaled smoke dosimeter was evaluated in our laboratory to determine the consistency of response to given amounts of smoke under both constant and intermittent flows. For various constant-flow conditions, a vacuum source was employed to withdraw smoke through the exposure-system cannula. To simulate animal-breathing patterns, a variable-phase large-animal ventilator was used to produce intermittent flows. The smoking machine generated smoke from experimental cigarettes, the particulate matter of which was collected immediately downstream of the cannula and subsequently analyzed for nicotine. Nicotine, considered to be the most reliable indicator of total smoke output, was compared with the response of the dosimeter. Results of these evaluation studies indicated that, under constant flow conditions at flow rates of less than 40 liters/min, the response of the dosimeter per milligram of nicotine is fairly constant. Apparent elevated responses at 40 liters/min and above were caused by reduced nicotine collection efficiency rather than by increased system sensitivity. Over a wide range of intermittent flows, the mean dosimeter response for cigarettes of a specific variety was 2004 ± 77 counts per milligram nicotine, or less than 4% relative standard deviation. This level of variability approximates that of smoke constituent deliveries from cigarettes smoked under standard conditions and suggests that variation in response of the dosimeter would not make an important contribution to inaccuracy in estimated inhaled-smoke dose.

Because laboratory evaluation of the dosimeter had indicated that response was proportional to the amount of smoke passing by the sensor over a wide range of flow conditions, the purpose of the field evaluation trials was to assess the magnitude of potential problems that might be associated with the use of the dosimeter on live animals. The field testing of the system was performed with male beagle dogs undergoing chronic tobacco smoke exposure at Borriston Research Laboratories, Temple Hills, Maryland.

One of the advantages of this instrumental approach is that it provides for the simultaneous visualization of animal-breathing patterns during smoke exposure. Some selected traces are depicted in Fig. 4.4. These traces represent the first measurements of this type made on beagles and are representative of the diversity of patterns observed. For example, dog 5083 was a very shallow breather, who succeeded in pumping smoke through the system without inhaling a large fraction of the smoke. The dosimetry measurement confirmed the visual observation. Dog 5041 was a fairly relaxed animal. The pattern of dog 5228 was typical of those that would occasionally exceed the linear response range of the pneumotach. We found that fogging of the smoke sensor with exhaled breath occurred infrequently and only to an extent of 0.1 to 0.2% of the sensor's full-scale response.

From the measured levels of smoke particulates inhaled during the field trials, a number of preliminary conclusions can be made. As expected, even within a given exposure, or targeted smoke dose group, there was considerable variation in the amount of smoke inhaled. Some of the animals were fairly consistent smoke inhalers, whereas others exhibited greater run-to-run variability. Some of the variability was a result of the manner in which the animals breathed, whereas some was due to differences in individual exposure-machine performance. Overall, individual animals were observed to inhale between 23 and 100% of the smoke particulates made available for inhalation.

Because it can be used to monitor continuously the respiratory patterns during smoking and the quantity of smoke particulates inhaled, this instrumentation will serve as an important extension to current procedures to quantify concentrated aerosol exposures in inhalation bioassays. The next phase of this work will be to provide for the determination of the amount of smoke actually retained and, thus, the "dose" achieved in the experiment. (*R. A. Jenkins, T. M. Gayle*[10])

Diesel-Fuel Obscurant Inhalation Bioassay Chemistry

Work is under way on a Department of Defense–funded activity (joint with the Biology Division), the

ORNL-DWG 79-15990R

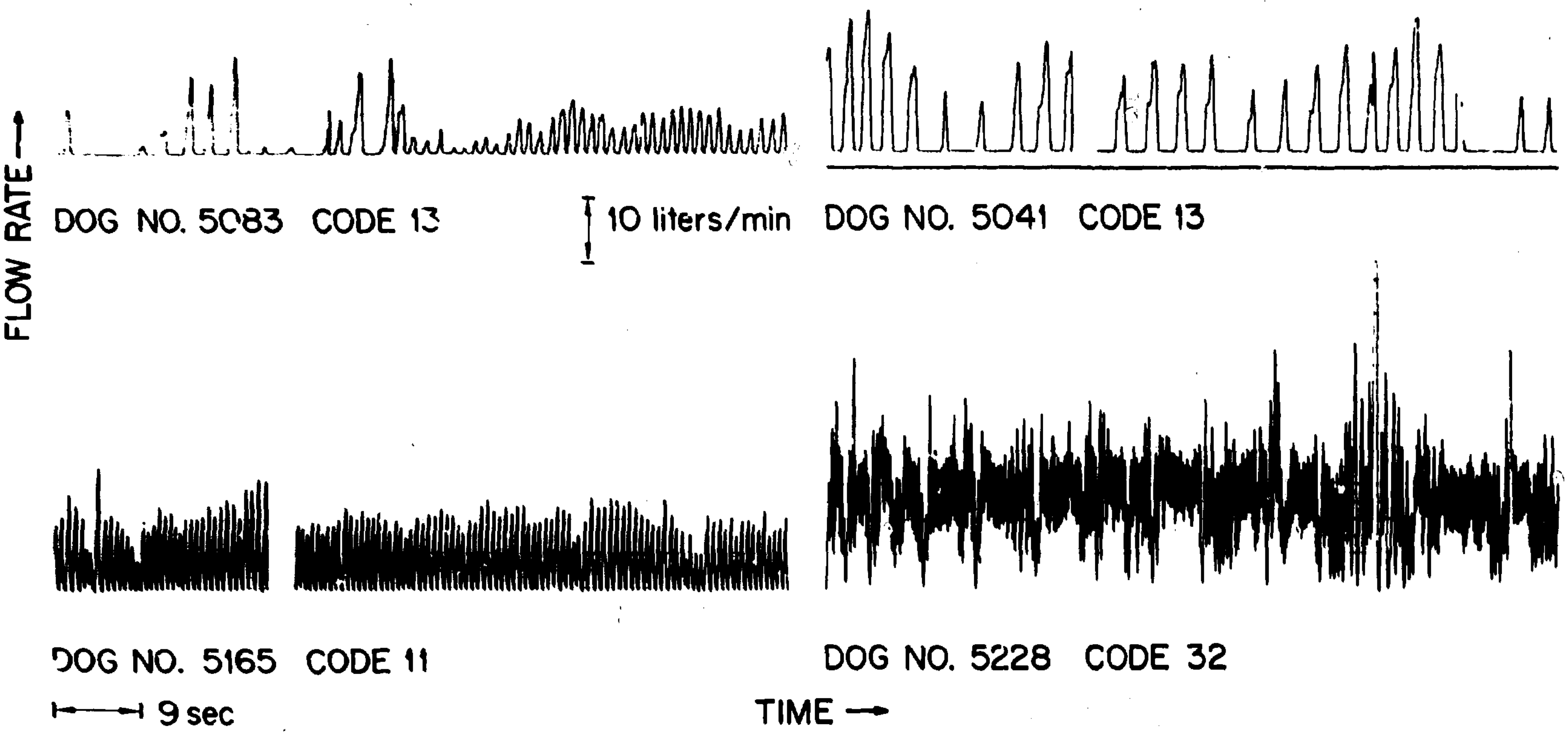

Fig. 4.4. Animal-breathing patterns during cigarette smoke exposure. ADL II exposure system with cuffed tracheal cannula.

purpose of which is to make a toxicological evaluation of a diesel-fuel obscurant (smoke screen) generated from an M-60 Army tank. We report here on developments directed toward the generation, monitoring, and chemical characterization of this aerosol.

The Army generates this smoke screen in practice by injecting diesel fuel into the hot manifolds of the M-60 tank. The fuel flash-evaporates, and the vapors are carried through the exhaust system by the exhaust gases, finally exiting into the atmosphere, where they rapidly condense to form a dense aerosol. Aerosol concentrations vary from 20 g/m^3 near the tank and diminish to 0.2 g/m^3 100 m downwind. The aerosol is very complex chemically. The predominant constituents are those of the diesel fuel, which is not well defined chemically and varies with its source. In addition, both the exhaust gases and the transformation products resulting from the interaction of these gases with the diesel fuel in the hot manifold add to the complexity. Physically, the aerosol is white, highly obscuring, and persistent in a still atmosphere. Particle sizes, although not well documented, are believed to be mostly below 1 μm.

It was not feasible to duplicate the real system for the proposed toxicological investigation. The alternative of driving the aerosol generator with a small diesel engine was also rejected, at least initially. In the time frame allotted for development before the biological exposures begin, it would be difficult to acquire, install, and test such an engine, let alone match its emissions with those of an M-60 tank, with any assurance of relevance. Instead, we proposed to begin by studying a "pure" aerosol of the diesel fuel, free of the complications introduced by the exhaust emissions.

A prototype generator for use in the initial phases of the biological investigation has been developed and is being tested. The generator is serving both as a development prototype for the model to be installed on the exposure chambers and as a source for investigations into the physics and chemistry of the aerosol. The aerosol is generated by an evaporation-condensation process by use of physical parameters that simulate those in the M-60 tank. The generator is constructed of 1-m-long 2.5-cm stainless steel tubing. A carrier gas (currently nitrogen) is introduced at one end and is heated to 600°C (typically) with an internal resistance heater. The fuel oil is metered into the hot gas, evaporates, and is carried down the tube. A secondary heater on the lower end of the tube maintains the vapor temperature sufficiently high (~350°C) to prevent premature condensation. The vapors are injected countercurrently into a glass condensation section (through which a large excess of air flows), mixed turbulently, and cooled to form the aerosol. The aerosol is then carried to appropriate chambers for study. Flow rates are adjustable and measured with rotometers. Temperatures are monitored and controlled by use of thermocouples. The generator has produced an aerosol of concentration of 10 g/m^3 at a flow rate of 0.4 m^3/min, conditions approximating those that will be used for the initial biological studies. At present, proportionately scaled-down flows are used to exhaust the aerosol into a 0.2-m^3 chamber for chemical and physical studies.

Preliminary particle-size-distribution measurements have been made by the use of a cascade impactor. Impaction samples were taken (1) from the flowing stream before its entry into the chamber, (2) from the chamber after the aerosol reached a steady-state concentration (~5 min), and (3) from the chamber, sealed and stagnant for an additional 15 min. The aerosol concentration was about 10 g/m^3. In all cases, most (>90%) of the material was collected on only two stages of the impactor. This result indicates that the aerosol had a low degree of polydispersity (geometric standard deviation less than 1.4) and that cascade impaction techniques will not be adequate to reveal the detailed shape of the size distribution. Nevertheless, one can estimate mass medium aerodynamic diameters from these data. They are, respectively, (1) 0.4, (2) 0.8, and (3) 1.4 μm. Under all three conditions, the particles are within the normally ascribed respirable limits, indicating that the generator will be adequate, from a particle size standpoint, for the bioassay. The increase in size from sample to sample parallels the age of the smoke cloud, indicating that the kinetics of coagulation and particle growth play a significant role.

It is important in the bioassay to be able to monitor aerosol concentration and homogeneity within the exposure chamber. On-line methods are much preferable to those that require analyses of grab samples. To this end, the Gayle/ORNL infrared particulate sensor has been adapted and calibrated for estimating diesel aerosol concentrations within a chamber. Response has been found to be linear from 3 to 20 g/m^3. Stability (zero drift on repeated or prolonged use) has been negligible. Response to stray light, if fluorescent, has been found to be sufficiently small that concentrations down to about 1 g/m^3 can be monitored, with minimal optical shielding. The response at constant concentration shows some particle-size dependence, but this dependence is sufficiently small that it will not detract from its usefulness, particularly in routine exposure use.

Chemical comparisons are being made between the aerosol generated at ORNL and that produced at Edgewood Arsenal by an M-60 tank by exhausting the aerosol into a wind tunnel. We sampled both aerosols with an apparatus consisting of an air-particulate filter pad, followed by a vapor-phase trap of Tenax resin and, finally, a Tedlar gas bag. Rough quantitation indicates that 5% of the aerosol is in the gas phase. The primary constituents of the particulate phase are paraffins in the C_{10} to C_{23} range, with a substantial fraction of unsaturated hydrocarbons, and many as-yet-unidentified chemical species. The more volatile species, for example hydrocarbons in the C_8 to C_{13} range, are found in the gas phase. There is significant variability in the chemical composition of diesel fuel, which will be reflected in the aerosol. Comparative chemical analyses of fuel, M-60-generated aerosol, and laboratory-generated aerosols are being emphasized in an attempt to understand the transformation processes that occur during aerosolization. (*R. W. Holmberg, J. H. Moneyhun, W. H. Griest, J. S. Wike*)

Analytical Methods for Human Cigarette Smoking Dosimetry

A significant impediment to understanding the health impact of smoking is the lack of an accurate assessment of the amount of smoke that a human retains. Because the amount of smoke generated, the chemistry of the smoke, and its deposition are governed by the manner in which a smoker puffs and inhales, a qualitative description of smoking behavior is not sufficient. Because instrumental dosimeters have the potential for influencing the smoke generation-inhalation process, determination of smoke constituents and/or their metabolites in physiological fluids offers a less invasive and potentially more accurate measure of the amount of smoke retained. Additionally, screening of physiological fluids may offer some insight into the metabolic impact of chronic smoke exposure. As an extension of our smoke dosimetry studies in animals, we have initiated a project to develop analytical methods for tobacco smoke constituents that may be quantitatively related to the retained smoke dose in humans. These methods will be directed toward specific smoke constituents and components uncovered as a result of chromatographic profiling of physiological materials.

These studies have three phases: the acquisition of a relevant sample, the development of a reliable analytical method for the marker compound, and the validation of this marker as a quantitative indicator of smoke exposure. Ideally, the sampling should be noninvasive, reproducible, and applicable to a wide variety of species. The marker compound should be plentiful but unique to tobacco smoke, and, if metabolized, done so in a similar manner over a wide range of dose levels. Initial validation studies would probably be performed on animals, with diet and other factors controlled.

Perhaps the most obvious choice as a marker is nicotine and its major metabolite, cotinine. Nicotine represents about 5 to 10% of the weight of particulate matter in cigarette smoke. Nicotine presence in humans arises from exposure to tobacco or tobacco smoke. Although several investigators have used serum nicotine concentrations to assess the pharmacological impact of smoke exposure, it has never been clear that observed levels of nicotine were quantitatively related to the smoke "dose." To determine what physiological fluid sample might be most appropriate for nicotine-cotinine determinations, we performed ^{14}C-nicotine tracer studies in collaboration with Borriston Research Laboratories (BRL) on male beagle dogs.[11] These studies indicated that 24-h urine samples offered the greatest promise of containing an amount of nicotine that could be quantitatively related to the amount of tobacco smoke retained by the animal.

A procedure was developed for the quantitative determination of nicotine and cotinine in urine.[11,12] Briefly, the nicotine and its metabolites are adsorbed from the urine onto XAD-2 resin, eluted, and analyzed by HPLC by use of absorbance detection at 254 nm. The method has proved to be simple and reliable. During the past year, the procedure has been adopted for routine use by the Addiction Research Foundation of Palo Alto, California, and the New York City Drug Abuse Laboratory. Investigators in Texas and Canada are also considering adoption of the method.

We are making attempts to validate the utility of urinary nicotine plus cotinine as a quantitative indicator of smoke dose. Levels in 24-h urine samples have been compared with estimated levels of tar deposition in the lungs of beagle dogs. Tar deposition was determined by radiochemical dosimetry.[13] Essentially, groups of beagle dogs were conditioned by exposure to tobacco smoke for 200 d at BRL. On the day immediately prior to the deposition experiment, a 24-h urine sample was obtained. To estimate the amount of smoke that an animal retains, the animal was exposed to the smoke of a cigarette that had been spiked with ^{14}C-dotriacontane. Immediately following exposure, the animal was sacrificed and its respiratory tract excised. Tissue samples were returned to ORNL for radiochemical analysis by tissue digestion and liquid scintillation counting. Results of these experiments showed that, as a group, the animals retained about 20% of the smoke particulates made available for inhalation.[14] However, individual doses achieved ranged from 1 to 40%. The urine samples collected were analyzed for nicotine and cotinine by the method described above. Results of the comparison of smoke deposition and urinary nicotine levels can be summarized. As a group, animals that had been exposed to the smoke of a low-nicotine cigarette had less nicotine in their urine. However, the relationship was not strictly proportional in that the group exposed to a ninefold higher level of nicotine had only a threefold higher level of nicotine and its metabolites in their urine. This result suggested that animals exposed to higher levels of nicotine may metabolize it much differently than animals exposed to lower levels. On an individual animal basis, there was very little correlation between the levels of nicotine in the urine and smoke deposition in the lungs. To determine if nicotine and its metabolites are, in fact, accurate quantitative indicators of smoke exposure, it will be necessary to make determinations that more accurately reveal the amount of smoke retained by the individual animal on the same day in which the urine samples are collected. Dosimetry instrumentation described elsewhere promises to achieve this determination.

Because it is present in tobacco smoke in relatively large quantities (1 to 5% v/v) and is excreted via a convenient route, CO in exhaled breath shows promise as a potential chemical dosimeter. Studies by other workers have indicated that CO levels in expired air are correlated with the fraction of circulating hemoglobin saturated with CO (i.e., percent COHb).

Existing instrumentation in the section, including both FTIR and our current method for measuring CO in smoke—GC with thermal conductivity detection—was surveyed and found to be too insensitive to measure CO at the levels expected in breath. However, instrumentation, based on proprietary electrochemical process that oxidizes CO to CO_2, is commercially available and has been purchased. The Ecolyzer, which is sensitive to parts-per-million concentrations of CO, is relatively unsusceptible to many chemical interferents. Initial evaluation of the system has indicated a very constant response to fixed levels of CO during periods of several hours. Initial experiments with potential interferences likely to be present in human breath indicated no response to high concentrations of O_2, CO_2, acetone, or methane. However, the system is very responsive to another common breath "pollutant," ethanol. We are trying to determine the maximum tolerable concentration of ethanol to which the system can be exposed.

For exhaled CO, obtaining a meaningful, reliable, and reproducible sample appears to be the chief analytical difficulty. The effect of various physiological factors, such as diet and respiration, on the rate of CO excretion may have to be determined. Because CO in the lower airway air may be diluted with air from the upper airways or trachea, a rigid breath sampling protocol may be necessary. This may make validation of a CO marker in an animal model more difficult, because animals cannot be instructed to breathe in a specified manner. Encouragingly, our preliminary experiments with smoke-exposed beagles at BRI, have indicated that CO concentrations in exhaled breath samples, collected without avoiding dilution by upper respiratory tract air, were roughly proportional to measured blood carboxyhemoglobin levels.

An initial scoping of human breath samples suggested that most nonsmokers have concentrations of 2 to 5 ppm CO in their breath. The smokers sampled had breath concentrations of 25 to 45 ppm CO. Interestingly, CO levels in the breath of the smokers do not seem to be proportional to the CO deliveries of their cigarettes, supporting the hypothesis that each smoker consumes a cigarette in a highly individual manner.

We have recently received pooled human urine samples from ORNL's Health Division. Comparisons of some chemical class fractions from the urine of smokers and nonsmokers have revealed substantial differences in the levels of as-yet-unidentified constituents. Again, sampling is an important problem, in terms of both relevance and availability. As specific constituents are identified, we expect to screen individual animal samples for presence of the identified constituents. If the components appear to be qualitatively related to either nicotine level or overall smoke exposure, we would expect to develop specific analytical methods for them. (*M. P. Maskarinec, R. A. Jenkins, B. E. Gill, J. E. Caton*)

Interlab Comparison of Analytical Methods for Cigarette Smoke Constituents

While continuing to develop new or improved analytical methods for the important constituents of tobacco smoke, we also have continued to act as a reference, or collaborating, laboratory. During the past year, these activities have been directed toward two of the gas phase constituents of smoke that are most biologically active, CO and the oxides of nitrogen.

Significant differences in smoke-constituent deliveries can often result from either normal cigarette-to-cigarette variability or minor changes in smoke generation or collection parameters. The greater the number of analytical determinations from a single smoke generation, the more reliable the determinations are likely to be. Also, because smoke generation often represents a substantial fraction of the time required for a set of determinations, reduction of the number of generations often results in increased sample throughput. This theory was the rationale behind our changing the gas phase collection procedure for the determination of CO in cigarette smoke. Previously, a separate generation was made on a single port smoking machine. Following filtration, the gas phase was collected in a Saran gas sampling bag. An aliquot of the sample was analyzed for CO by gas-solid chromatography.[15] Usually, four to six determinations comprised an analysis for a given brand of cigarettes. Precision of the determination was about ±6%. Modifications in the exhaust valving of our four-port Phipps and Bird analytical smoking machine permitted us to collect the gas phase from four smoking stations (in individual collection bags), while simultaneously collecting particulate matter on filters for the usual tar and nicotine determination. Because the conventional procedure is to smoke four cigarettes sequentially, each gas phase sample that was analyzed represented the average of four cigarettes. These changes have resulted in a significant improvement in both the accuracy and precision of the CO analysis. Because the new sampling procedure provided for a more complete collection of the critical last few puffs of the cigarette, apparent CO deliveries increased by about 20%. Also, the increase in the number of cigarettes comprising the samples resulted in a 50% reduction in the relative standard deviation of the average CO deliveries.

We were requested to provide background data for CO deliveries of U.S. commercial cigarettes in support of conclusions in the recently released Surgeon General's Report on smoking and health. In response to that request, we surveyed over 120 of the more popular brands of U.S. commercial cigarettes for tar, nicotine, and CO. The cigarettes were obtained from the Federal Trade Commission's (FTC) supply of cigarettes sampled from 50 different locations in the country. Deliveries of constituents per cigarette ranged from 1 to 29 mg CO, 1 to 36 mg tar and 0.1 to 2.0 mg nicotine for the 120 brands analyzed.[16,17] One of the more interesting findings was that, in general, for cigarettes having a given tar delivery, the filtered brands delivered substantially more CO than the nonfiltered varieties.

The federal government is currently considering requiring the inclusion of the amount of CO delivery in cigarette advertising, in a manner similar to that now required for "tar" and nicotine deliveries. The FTC is currently developing an automated instrumental procedure to determine the presence of CO in massive numbers of commerical cigarettes. Because the ORNL study represented the first publicly available survey by brand for the presence of CO in U.S. commercial smoking products, the FTC used the data as a standard for comparison with its initial results. Another National Cancer Institute (NCI) Smoking and Health Program contractor has also used the data for comparison purposes. Because initial comparisons showed substantial disagreement between the two sets of data, we were requested to provide information and assistance to that contractor concerning sampling and analytical methods. In a subsequent round-robin CO analysis on six brands of commercial cigarettes, all three laboratories were in good agreement on all but one brand. As a result of this work, the contractor laboratory has now adopted our sampling and analysis procedure.

Oxides of nitrogen (NO, NO_2, NO_x) are also important. Previously, we had reported the development of a procedure employing a commercially available chemiluminescent analyzer and a selective trapping material for the determination of NO and NO_x ($NO_2 = NO_x - NO$) in cigarette smoke.[18,19] We found that there was considerably more NO_x present in fresh cigarette smoke than had been previously reported. This resulted from the more rapid analysis of the smoke that the chemiluminescent procedure affords, preventing side reactions with organic-gas phase constituents, and from a more efficient smoke collection procedure. We had initially reported that a larger-than-expected fraction of the NO_x was present as NO_2.[18,19] Work completed during this past year involved further investigation of the latter phenomenon. These recent studies revealed that we had been in error. Most of the apparently high level of NO_2 was really an artifact of the aging of a fraction of the smoke puff entrained within the dead volume of the smoking machine between puffs. The aging permitted NO to be converted to NO_2 by reaction with O_2 in the smoke. Substitution of the conventional smoking machine with a special low-dead-volume machine reduced the opportunity for smoke aging. The new machine resulted in a lowering of the apparent level of NO_2 in the smoke to the point where, in most cases, the level of NO_x was statistically indistinguishable from that of the NO. These studies continued to confirm, however, that the concentrations of NO in cigarette smoke were considerably larger (by 50 to 100%) than those determined by other analytical methods.

Because the levels were so high, several investigators have been interested in verifying the efficiency of the chemiluminescent procedure, using their own commercial analyzers. Results of these collaborative studies, in which fresh smokes from cigarettes have been generated at each laboratory and immediately analyzed, have been mixed. In a comparative study with investigators at a cigarette industry laboratory, values for NO_x deliveries averaged about 25% lower than those determined at ORNL for seven widely different types of cigarettes. Discussions with these investigators suggested that the apparently lower NO_x deliveries may be due to the 15-s time period that the undiluted smoke gas phase was allowed to stand prior to analysis. During this time period, side reactions of the NO_x with organic gas phase constituents could occur that would act to diminish the NO_x levels. The procedure that we use avoids this difficulty by diluting the smoke within 2 s after generation and completing the analysis within 8 to 10 s. In comparing observed levels of NO in the smoke of a reference cigarette, investigators at another laboratory obtained values within 5% of those determined at ORNL. Those investigators used a method very similar to the one we use and substantially diluted the gas phase of the smoke immediately after generation. Currently, we are using smoke of commercial cigarettes and are comparing the levels of NO_x that were determined by the chemiluminescent procedure with values obtained by classical wet-chemical methods. These data should provide relative ratios of NO_x deliveries so that a reference point can be maintained when NO_x values are determined solely by chemiluminescent procedures. (*R. A. Jenkins, R. B. Quincy, B. E. Gill*)

Advances in Glass Capillary Gas Chromatography

The rapidly expanding use of glass capillary columns for GC analysis is evidenced by the fact that several other divisions at ORNL have requested our assistance in the use of this technology. During this year, we have completed several studies aimed at improving both the inertness of the columns and their thermal stability. These studies have focused on the preparation of the glass surface for optimum interaction with the stationary phase.

Surface modifications fall into two general categories: physical and chemical. Physical modifications depend on the nature of the glass. Soda-lime glass, with its relatively high alkali content, can be treated with dry HCl gas at elevated temperature. This treatment results in reaction with the alkali to form salts on the surface. Depending on the temperature and concentration of HCl, this surface may be varied considerably. When low HCl concentrations at 350° are used, cubic crystals are formed. If the HCl concentration is high and the reaction is carried out at 400°C, the surface will be completely covered with fine salt particles. Electron micrographs of this surface reveal contouring and cratering. This contoured surface both deactivates the glass (removing or covering Lewis acids and bases) and improves the wettability of polar stationary phases. It is not, however, a suitable surface for nonpolar phases.

The low alkaline content of borosilicate glass makes salt deposition impossible. Borosilicate glass is, however, inherently more inert and of higher purity. In addition, a physically smooth glass surface is ideal for the deposition of nonpolar stationary phases. We have developed and published[20] an acid-leaching technique that removes the remaining adsorptive sites and produces a surface of essentially pure silica.

A major effort has been directed toward characterizing the chemical deactivation of the surface. This chemical deactivation is a result of the presence of Si-OH (silanol) groups on glass surfaces. Silanol groups can be reacted with various trialkylsilanes to incorporate functionality similar to that of the stationary phase. This reaction is crucial to the stability of the coated column. The traditional silylation reaction involves hexamethyldisilazane (HDMS), with trimethylchlorosilane (TMCS) as a catalyst. We have completed a study of the mechanistic considerations of the reaction of surface silanols with various reagents. The addition of TMCS to the reaction medium results in the formation of ammonium chloride. We were able to detect this compound on the surface of glass capillary columns silylated in this manner (both soda-lime and borosilicate). This finding is of little importance, unless one considers that ammonium chloride dissociates at 300°C to form ammonia and HCl. These compounds are, at the least, detrimental to the surface-stationary phase interaction. We therefore increased the temperature of the reaction and eliminated this catalyst. Reaction conditions at this time are: pure HMDS under dynamic conditions at 270°C. These conditions have resulted in columns of high efficiency, good inertness, and greatly improved thermal stability. The thermal limit of the stationary phase is now the determining factor in the maximum operating temperature of the column. For example, the thermal limit of Dexsil-400 columns has been increased from 320 to 375°C by the use of these reaction parameters, and the lifetime of the column is increased. This work will be published.[21]

We have also studied liquid crystal stationary phases for glass capillary GC. Liquid crystals are highly ordered arrays of planar molecules that afford the ability to develop separations based on steric interactions between solutes and the stationary phase. Because liquid crystals do not interact with glass surfaces in the same way as polymeric stationary phase materials, it was necessary to study and to develop column preparation techniques and column performance. This work has been done, and we have been able to separate geometric isomers that had not been resolvable by other means. Thus, liquid crystals appear to offer an advantage wherever highly selective and specific separations are needed. A manuscript describing this work has been prepared.[22] (*M. F. Gonnord,*[23] *M. P. Maskarinec*)

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5. Nuclear and Radiochemical Analysis

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The Nuclear and Radiochemical Analysis Section provides analyses and development support for ORNL and UCC-ND programs in radioanalytical chemistry and activation analysis. The section has three groups, Radiochemical and Activation Analysis, Low-Level Radiochemical Analysis, and Special Projects. All three groups perform work that ranges from routine radiochemical analysis to short-term development projects. Long-term development and research studies are mainly concentrated in the Special Projects Group. Over the past year, there has been a general expansion of the work performed by the section. Sample analysis, in support of the DOE-sponsored programs, increased approximately 20% during the year, new development projects were initiated, and efforts to upgrade capabilities were continued.

The acquisition and utilization of new facilities and instrumentation have received considerable attention this year. New laboratories and a counting room for low-level radiochemical analysis were put into full operation to support expanding ORNL programs requiring analysis of radionuclides in environmental materials. A new Nuclear Data 6603 (ND 6603) spectrometer system was installed and is presently being used to acquire and process data from six alpha- and three gamma-ray detectors. Three new high-efficiency lithium-drifted germanium detectors were put into operation to perform low-level gamma-ray spectrometry on environmental materials. Addition of the spectrometry system and detectors has greatly increased capabilities for general low-level analysis. In the Radiochemical and Activation Analysis Group, a new intrinsic germanium x-ray detector was placed in operation, and an existing spectrometer system (ND 6620) was expanded by the addition of more memory, another input/output terminal, and other electronic components. Plans were completed this year for renovation of chemical laboratory and counting facilities of the Radiochemical and Activation Analysis Group, but the plans have not yet been implemented.

Several new development projects were initiated within the section this year. A study of the possible use of Cerenkov counting for analysis of low levels of beta-emitting radionuclides has yielded results that indicate that environmental ^{90}Sr analysis can be made by a simple, sensitive method involving Cerenkov counting of the energetic beta emitted by the ^{90}Y daughter of ^{90}Sr. A neutron activation analysis method for ^{99}Tc in reactor fuel solutions and gas traps was developed and has been used to study the behavior of technetium in reactor fuel reprocessing operations.

Interest in ^{99}Tc in the environment near nuclear facilities has continued, and a radiochemical separation method was devised for isolation of ^{99}Tc from environmental matrices prior to low-level beta counting. A project was initiated with the Mass and Emission Spectrometry Section to prepare ^{97}Tc for isotope dilution mass spectrometric analysis of ^{99}Tc at very low concentration levels. Development and sample analysis assistance is being given to the IBM Corporation in a program to determine the effect of alpha-emitting uranium and thorium impurities on the frequency of "soft errors" in semiconductor memory devices. An investigation of the transport of radionuclides in surface streams, as a function of stream flow rate, is nearing completion. A study is under way to determine the quantity of gamma-emitting radionuclides in animals living on the Oak Ridge reservation. This study involves low-level analysis of tissue sample from road-killed deer and in-laboratory analysis of trapped, live mammals from the area.

Over the past year, the section has responded to several emergency situations. Immediately following the reactor failure at Three Mile Island (TMI) in March 1979, the section was involved in the initial assessment of releases of radioactivity to the environment of TMI. This involvement has continued through participation in a multidivisional effort to assist the Nuclear Regulatory Commission and Metropolitan Edison Corporation in evaluation of the incident and in the estimation of the extent of contamination of the TMI reactor containment building. Another emergency situation involved the possible failure of an earthen dam of a holding pond containing low-level radioactive waste. The section provided low-level radiochemical analysis of the pond water and sediments in evaluation of the situation and monitored radioactive releases during repair operations.

RADIOCHEMICAL AND ACTIVATION ANALYSIS

Sample Analysis Program

The Radiochemical and Activation Analysis Group provides radiochemical and multielement analysis in support of various ORNL programs. Most of this support is for the Chemical Technology, Industrial Safety and Applied Health Physics, Solid State, Environmental Sciences, Engineering Technology, and Engineering Physics divisions and other UCC-ND facilities. We provided gamma-ray spectrometry and radiochemical analysis support for the TMI incident and uranium and thorium analysis in semiconductor and related materials for IBM. Our decontamination studies of coated reactor component specimens have taken on additional significance since the TMI accident. Over 24,000 radiochemical analyses were made this year on a variety of materials.

This year the demand for multielement and uranium analyses increased 35%. Uranium determinations for the National Uranium Resources Evaluation (NURE) program accounted for the major part of the increase. About 600 samples from a special study by the Bendix Corporation were submitted through the NURE program, and the total sample load from the NURE program was about 18,000 this year. Multielement and radioisotope analyses totaled 12,900. Multielement analyses were performed on coal, fly ash, sediments, coal fractions, honey combs, bees, insects, pollen, falcon feathers, graphite, crude oils, mineral wool, MgO, SiO_2, and industrial diamonds. Radioisotope products analyzed were ^{153}Gd, ^{56}Co, ^{237}U, ^{75}Se, ^{119m}Sn, ^{57}Co, ^{37}Ar, $^{141-144}$Ce, ^{95m}Tc, ^{237}Pu, $^{66-67}$Ga, and ^{113}Sn.

We received a number of water samples from TMI for analysis. These samples were analyzed to establish and/or to verify levels of contamination of reactor cooling water and wastewater from storage tanks and to assist in the evaluation of proposed cleanup operations. Gamma-ray spectrometry was used to determine gamma-ray emitting fission products; ^{89}Sr and ^{90}Sr were determined by radiochemical separation and counting procedures, and ^{3}H was separated and determined by liquid scintillation counting. A sample received in late August was analyzed for ^{129}I by our new neutron activation analysis (NAA) procedure. The painted surface of a 7-cm steel disk, cut from the containment building wall, was also analyzed. The total activity of each radionuclide was determined first, and then the disk was cut into pieces for decontamination tests. An overall decontamination factor of 4 was obtained. *(J. F. Emery, L. C. Bate, A. R. Crook, L. M. Jenkins, H. A. Parker, L. R. Hall, K. J. Northcutt, S. H. Prestwood, J. W. Wade)*

Use of the Sample Transaction System in the Radiochemical and Activation Analysis Group

The Sample Transaction System (STS) is a data management program developed by the Computer Sciences Division. It resides in the DEC 10 computer at ORNL and is used by several groups within the Analytical Chemistry Division. At the Intermediate Level Radiochemical Analysis Laboratory (ILRAL), all groups of samples are given work request numbers, by which all data are reported and filed. When all of the analyses on a work request are completed, two computer reports are automatically printed. After proofing, one is sent to the requestor, and the other is filed with the laboratory data. The computer data are held for four weeks before being dumped to microfiche. Two microfiche copies are kept for ten years; however, the file folder is kept for only three years and then is discarded. Each day a backlog of all pending work is printed for use in work scheduling and sample inventory. These features (sample inventory, computer reporting, and backlog generation) meet the needs of our laboratory. We are now interfacing the data management terminal (Tektronix) 4025) to the ND 6620 analyzer computer to afford direct transfer of data between the analyzer and the DEC 10. *(L. M. Jenkins)*

Gamma-Ray Spectrometry at the Intermediate Level Radiochemical Analysis Laboratory

Gamma-ray spectrometry at the ILRAL supports a diverse assortment of programs at ORNL. This technique is used to analyze fission product mixtures for the Chemical Technology Division's nuclear fuel reprocessing studies, to assist with reactor flux mapping, and to identify radionuclides in the Operations Division's stack monitoring system. On-line data reduction of gamma-ray spectra provides fast and accurate analysis of TMI samples. Recently, coal and fly ash have been analyzed for radium in support of ORNL's Coal Conversion Technology program. To provide consistently high-quality data in a reasonable time frame, continuing efforts have been made to improve equipment, instrumentation, and software, as well as the level of staff training.

We have investigated ways to reduce background levels inside the refrigerator shields of our germanium detectors. All of the shields had their inner lead scraped and their copper-cadmium liners polished. The addition of steel liners reduced specific peaks attributable to naturally occurring thorium and uranium but increased the low energy baseline from backscattering. Therefore, steel liners were not installed. Placing lead brick under the detector assemblies reduced ^{40}K by 40%. Lining the detector hole in the shield with cadmium plate reduced lead x rays by 50%. A clean air line was installed in the counting room to continuously purge the air inside the detector shields; this resulted in a 15% reduction in uranium and thorium daughter radioactivities.

A live time corrector and pulse pile-up rejector, Canberra Model 1468, has been installed to provide greater versatility in counting samples of high count rate. An additional analog to digital converter, Nuclear Data Model 575, has been purchased to be used for a proposed alpha pulse height analysis system. In our efforts to more fully utilize the computer aspect of the ND 6620 analyzer, we have purchased three logic boards to be used in interfacing other devices, such as the Packard liquid scintillation counter, to the ND 6620. Also, a Princeton Gamma Tech intrinsic germanium x-ray detector has been acquired and installed on the ND 6620.

Software is a major part of any computer-based system, and we have made major strides in the area of software acquisition and use during the past year. A Decscope terminal has provided much-needed access for computer program generation and testing. Six members of the staff attended an 8-h introductory course in the operation of the ND 6620 analyzer, and three members attended a full one-week course in Basic and Fortran programming taught by Nuclear Data.

A major effort has begun to utilize the full power of the ND 6620 computer-based data acquisition system for both routine and developmental work. Although Nuclear Data-supplied software is adequate for most manual data acquisition and analysis tasks, manual processing is prone to error and is a highly inefficient use of both personnel and equipment. A variety of programming tasks was undertaken with the common goals of efficient use of equipment and operator time while increasing quality assurance. These tasks have been highly successful, and further improvements are being made on a continuing basis.

Three job streams (command files) were written to handle the data acquisition, to dynamically allocate system resources, and to perform data analysis for virtually every gamma-ray spectrometric analysis performed by the ILRAL. One command that may be scheduled for any time in the future has replaced more than 20 commands, which had to be entered in correct order over a 7-min period. Data acquisition and processing may proceed reliably now even when an operator is not in attendance. Multiple entry points provide a high degree of flexibility, so that special samples can be handled routinely.

Several Fortran programs have been written to aid in error detection. Programs now routinely write the user's logical unit assignments (i.e., the run time configuration) on the sample report. On termination of a job stream, another program verifies that logical units have not inadvertently been reassigned. Also, a special error flag, set by Nuclear Data-written programs, is checked for possible execution errors. A special sequence number, used to identify spectral data files on magnetic tape, is written on the sample report by a user-written program. This has eliminated problems associated with retrieving spectral data from magnetic tape.

By the use of several programs, the time required to report results has been significantly decreased. Chlorine and iodine values obtained by NAA are now calculated with two user-written programs. Conversion of results from microcuries to disintegrations per second is provided by another program, because the original Fortran source codes were not available for modification. Decay corrections are also made where Nuclear Data software fails to do so. Automatic background subtraction for low-level samples is provided by a program written by N. H. Cutshall (Environmental Sciences Division) and modified to fit our needs. With these programs many time-consuming, repetitive, and error-prone hand calculations are eliminated.

Software has been developed to allow use of the ND 6620 for batch processing after regular working hours. The ND 6603 system used by the Low-Level Radiochemical Laboratory has limited data handling capabilities. Although spectral data files written on magnetic tape by the ND 6603 can be processed by the ND 6620, too much operator time is required, and the instrumentation usage is inefficient. Accordingly, programs were developed to allow fully automatic processing of up to 120 spectral files, with little user interaction. Sample parameters for all samples are entered at one time. A job stream reads the magnetic tape, updates sample parameters, assigns the correct logical units for that sample, and performs all routine data processing. The processing can continue overnight or for as long as required. Data acquisition for overnight counts can proceed concurrently. Thus the system is efficiently used with no operator present.

Current work includes evaluation of a Nuclear Data-written NAA software package. While extending the capabilities of the system somewhat, the NAA software may require additional programming support. Other work under development includes a series of programs that will accept paper tape output from a Packard Model 2405 liquid scintillation counter for processing by the ND 6620. The ND 6620 will perform all calculations, print a summary report, and, eventually, format results for direct submission to the STS on the DEC 10. Modular programming techniques will allow this system to accept data directly from the Packard Model 2405, with a minimum of programming effort when the instruments are directly connected. This process will result in faster calculations and eliminate key punch errors altogether.

The programming efforts of the last year have given the ILRAL a powerful analytical tool tailored to the exact needs of the user. It is a system that is well integrated into the Laboratory environment and is flexible, reliable, and capable of responding to future needs. *(A. R. Crook, J. F. Emery, L. M. Jenkins)*

Research Applications of Neutron Activation Analysis

The advent of high levels of integration in computer memories has created an intense interest in trace levels of alpha impurities in silicon and other related materials. For *n*-channel Metal Oxide Substrate (MOS) random-access memories (RAMs) and charge-coupled devices (CCDs), the charges are electrons, and capacitors take the form of potential wells in the *p*-type silicon under positively charged polysilicon gate electrodes. Alpha particles interact with silicon by generating electron-hole pairs; these can be collected by depletion layers such that the generated electrons end up in storage cells. If enough electrons are trapped, then a soft error results. As little as 1 to 2 ppb of uranium or thorium can create soft errors that are significant in current RAMs. We are involved in a program with IBM to determine uranium and thorium in silicon and other related materials. Current levels of uranium and thorium in silicon range from <5 to ~ 80 ppb and as high as 300 ppb in aluminum. We are developing a quality control program for uranium in the low-ppb range. Our present quality control program operates in the range of a few parts per million.

A study of trace elements in human lungs has been initiated recently. This study is being done at the neutron activation analysis facility at ORNL's High Flux Isotope Reactor (HFIR). Postmortem samples of lung tissue come from a highly industrialized area in Ohio. The samples are ashed in an oven at 290°C, after which the ashes are placed into irradiation vials and weighed. After a sample has been irradiated for 3s, a count is made within 2 to 4 min and again within 1 to 2 h to determine nuclides with short half-lives. These samples are then reirradiated for 300 s and permitted to decay for a week. One- and two-week post-irradiation counts are taken to determine the presence of nuclides with half-lives greater than 20 h and 200 h respectively. Statistical and pattern recognition studies are contemplated for possible correlations between trace elements and pathology of former factory workers. Similar studies on a control group consisting of individuals from the same industrial area but having no history of factory-type work environment are also under way. *(G. R. Norris,*[1] *L. C. Bate, J. F. Emery)*

Development of Methods for Analysis of ^{99}Tc and ^{14}C in Reactor Fuel Solutions

A method for the determination of ^{99}Tc by neutron activation analysis in fission product solutions was developed and has been in routine use for eight months. In the method, ^{99m}Tc or ^{95m}Tc is added prior to the separation to correct for chemical yield. The ^{99}Tc in the sample is extracted into cyclohexanone from a basic carbonate solution. Technetium-99 is stripped into water by the addition of carbon tetrachloride to the cyclohexanone phase. A final step in the separation procedure is adsorption of ^{99}Tc on an anion exchange column that provides additional decontamination and places the ^{99}Tc in a concentrated form for neutron activation analysis.

Neutron irradiations of the isolated ^{99}Tc are made in the pneumatic tube facility at the HFIR at a flux of 5×10^{14} neutrons s^{-1} cm^{-2} for 11 s. Induced ^{100}Tc radioactivity is determined immediately after irradiation by the use of gamma-ray spectrometry to measure the 540- and 591-keV lines. Sensitivity of the analysis under these conditions is approximately 5 ng, and samples of up to about 100 ml volume are easily processed. The method has been successfully applied to reactor fuel solutions and off-gas traps containing 6.5×10^{-4} to 240 μg of ^{99}Tc per milliliter. This work is being published in the Proceedings of the Twenty-Third Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tennessee, October 9–11, 1979.

The gas adsorption train used in the separation of ^{14}C from reactor fuel solutions has been redesigned to reduce the time required for analysis. The volume of the reaction tube and water trap has been reduced to expedite the CO_2 transfer to the hyamine traps. This has resulted in a decrease of analysis time from 2 h to about 20 min. The CO_2 and carrier gas is drawn under vacuum through the gas adsorption train from the reaction tube and past the hyamine trap. This procedure ensures that any gas leak in the system will be inward, with no loss of the ^{14}C. The improved $^{14}CO_2$ gas train has been placed in routine use. A report describing the improved apparatus and the method of operation is in preparation. *(L. C. Bate)*

Quality Assurance in Radiochemical and Activation Analysis

The bench manual of radiochemical procedures has been updated with new methods for ^{129}I, ^{99}Tc, and ^{14}C. A new ^{129}I standard has been procured from Amersham Corporation to replace the old National Bureau of Standards (NBS) ^{129}I standard, which was almost depleted. Aliquots of this standard are run with each series of samples. A set of sealed liquid scintillation standards was obtained for monitoring the performance of the liquid scintillation counter. These standards were put into service in July. Since then, the average standard deviation for ^{3}H has been improved to 0.8%. The standard deviation for ^{14}C and ^{36}Cl standard counts is approximately 0.3%. In addition, NBS ^{14}C and ^{3}H standards are analyzed with the samples as a routine quality control procedure.

Our gamma-ray spectrometry systems are calibrated with mixed radionuclide sources from NBS and Amersham and monitored with NBS ^{60}Co sources for changes in efficiencies. Assistance was given NBS in measuring ^{60}Co in several samples. In the course of this work, samples and standards were measured twice by Ge(Li) spectrometry at NBS and by Ge(Li) and the gamma ionization chamber at ORNL. The overall average standard deviation was 1.2%, which is considered very satisfactory.

Quality assurance in multielement neutron activation analysis is accomplished by periodically analyzing the NBS standards of coal, fly ash, and orchard leaves. Uranium analysis by delayed neutron counting has blind controls submitted through the NURE program, and NBS coal and fly-ash standards were used. Aliquots of an NBS SRM-930 uranium standard are used for calibrating the system. *(J. F. Emery, S. A. Reynolds)*

LOW-LEVEL RADIOCHEMICAL ANALYSIS

Analysis of Statutory Samples

Approximately 25% of the analytical effort in the Low-Level Radiochemical Analysis Group is committed to the analysis of statutory samples that are submitted by the Operations and the Industrial Safety and Applied Health Physics divisions.

The Operations Division routinely submits monthly composited samples that are analyzed for ^{90}Sr, gross alpha, and gross beta activities. The monthly suite of samples comprises 25 aqueous solutions taken from locations within the ORNL operating area. Quite frequently the personnel of Operations submit special samples that are taken either to verify abnormal releases or to locate the sources of releases; analysis of these samples requires short turn-around time, so that any necessary actions can be taken. In general, the activities in all of these samples range from the detection limits (0.01 dis min^{-1} ml^{-1}) to approximately 500 dis min^{-1} ml^{-1}. Table 5.1 lists typical results for a monthly set of samples from the Operations Division.

The Industrial Safety and Applied Health Physics Division submits a variety of materials collected over several time periods (week, month, quarter, semiannual, and year). Weekly collections include water samples from White Oak Dam and White Oak Creek and charcoal cartridges from 19 stations in and around the ORNL operating area. The water samples require ^{90}Sr and ^{131}I analyses that are performed by large-volume radiochemical separations; also required are ^{3}H and gamma analyses that are performed by nondestructive methods [i.e., ^{3}H is counted by liquid scintillation and gamma emitters are determined by gamma-ray spectrometry with Ge(Li) detectors]. The charcoal samples are analyzed for ^{131}I by gamma-ray spectrometry, using either NaI or Ge(Li) detectors. Water samples from White Oak Dam and White Oak Creek are composited for a month and analyzed for the same constituents as are the weekly collections. Quarterly composite water samples taken from several locations on lakes and streams are analyzed for gamma emitters. Quarterly composite air filters are analyzed for ^{90}Sr, Pu, U, and Th isotopes by sequential radiochemical separations and low-background beta and alpha counting. Biota samples, fish, and vegetation are analyzed for ^{90}Sr, Pu, U, and Th isotopes on quarterly, semiannually, and yearly collections. Table 5.2 lists typical concentrations of the various samples analyzed for the Industrial Safety and Applied Health Physics Division. *(T. G. Scott, G. I. Gleason,[2] P. S. Gouge, C. C. Granger, C. V. Holmes, W. C. Massey, N. A. Teasley, A. J. Weinberger)*

Table 5.1. Typical concentrations in monthly composite water samples, (dis min^{-1} ml^{-1})

Sample location	Gross alpha	Gross beta	^{90}Sr
Flume	0.02	0.25	0.07
Melton branch 1	0.02	2.8	1.0
White Oak Creek	0.05	0.76	0.18
Equalization basin	1.4	82	43
Column station 4	2.5	15	0.48
Bridge at Building 7500	0.08	1.1	0.21
Homogeneous reactor test	0.05	2.7	0.75
Melton branch 2	0.05	0.08	0.02
Sewage treatment (week 1)	0.01	2.3	0.65
Sewage treatment (week 2)	0.04	2.0	0.65
Sewage treatment (week 3)	0.05	1.4	0.61
Sewage treatment (week 4)	0.04	1.8	0.66
Man hole 240	0.49	0.60	0.08
Man hole 25	0.32	2.8	1.1
Man hole 112	0.41	27	4.0
Man hole 114	0.85	570	320
Man hole 234	0.23	68	28
Man hole 235	1.2	0.82	0.07
Man hole 149	0.03	1.8	0.40
Man hole 190	0.05	0.09	0.01
Man hole 229	0.13	1.1	0.19
Man hole 243	0.25	175	87
Man hole 190d	0.01	0.18	0.03
Pump station 1	9.1	390	195

Table 5.2. Typical concentrations of radionuclides in environmental materials, pCi/g or pCi/filter

Matrix	^{241}Am	^{239}Pu	^{238}Pu	^{238}U	^{234}U	^{232}Th	^{228}Th	^{90}Sr	^{131}I
Water	0.01	0.01	0.001	0.01	0.01			0.20	0.02
Soil	0.3	0.5	0.002	0.4	0.4			2.5	
Filter 1		2.0	0.25	75.0	90.0	1.5	2.5	50	
Filter 2									10
Vegetation	0.005	0.002	0.001	0.2	0.2	0.05	0.08	1.0	
Tissue	0.01	0.004	0.002	0.1	0.1			2.0	

Radioanalytical Support for the Environmental Impact Program

In February 1979, the Industrial Safety and Applied Health Physics Division began to evaluate the environmental impact of the ORNL operations over a one-year period. Initially, three sets of samples, comprised of more than 300 water samples per set, were taken along White Oak Creek and its tributaries within the operating area. These samples were analyzed for ^{3}H and pH; on completion of these analyses, the samples were stored for possible further analyses.

Subsequent water samples have been taken to evaluate the effects of high-flow conditions in White Oak Creek and in particular at White Oak Dam. During high-flow conditions, samples were taken at a rate relative to the flow over White Oak Dam; soon after being taken, the water samples were filtered through 1-μm Millipore filters to separate the particulates. Subsequently, the two fractions of the samples were analyzed for gamma emitters by Ge(Li) gamma-ray spectrometry and for ^{90}Sr by radiochemistry on large volumes of samples; ^{90}Sr and ^{60}Co are found to be dominant in the liquid, and ^{137}Cs is dominant in the particulate material.

Future plans call for the radioanalysis of soils, sediments, and biota samples. *(T. G. Scott, G. I. Gleason,*[2] *P. S. Gouge, C. C. Granger, C. V. Holmes, W. C. Massey, N. A. Teasley, A. J. Weinberger)*

Waste Management Program Sample Analysis

During the past year, we have provided analytical support for the Environmental Sciences Division as they conduct studies on waste burial sites. These studies are a portion of the Waste Management Program, which has the overall objective to evaluate and monitor the radioactive contamination contributed by burial sites to ORNL discharges. Work related to the Waste Management Program constitutes approximately 25% of our analytical efforts and involves the analysis of a variety of materials from several of the burial grounds and trenches. Three principal investigators in the Environmental Sciences Division have submitted samples of soil, sediment, water, and biota that required approximately 2000 radiochemical analyses.

In one of the investigations,[3] samples were collected from a spoil area and from burial ground number three (BG-3), both of which are west of the ORNL operating area, to determine what effects these two sites had on the effluent drainage systems. Soil, surface water, and groundwater were the principal materials that were submitted for radiochemical analysis for ^{90}Sr, ^{239}Pu, ^{3}H, ^{241}Am, and gamma emitters. Seventy grams of soil and 900 ml of water were utilized for nondestructive Ge(Li) gamma-ray spectroscopy in determining the gamma emitters. Ten grams of soil and 250 ml of water were subjected to low-level radiochemical procedures for the determination of ^{90}Sr, ^{239}Pu, and ^{241}Am.

Soil samples were transferred to petri dishes and counted for 1 to 16 h with Ge(Li) detectors. Cesium-137 was found to be the dominant gamma emitter and varied in concentration from 0.1 to 500 pCi/g. Hot nitric acid leaching was used to extract the radionuclides from the soil prior to sequential separations and purifications. Concentrations in the order of 200 pCi/g for ^{90}Sr, 100 pCi/g for ^{239}Pu, and 10 pCi/g for ^{241}Am were found. Water samples were transferred to Marinelli beakers and counted for 4 to 16 h with Ge(Li) detectors to assay gamma emitters; ^{90}Sr and the actinides were determined by large-volume radiochemistry. In general, the concentrations of radionuclides in the water samples were one to two orders of magnitude lower than those found in the soils.

The results of the study of BG-3 generated sufficient interest to bring about remedial actions, and results from the study of the spoil area gave evidence of low-level discharges to Raccoon Creek, which had not previously been monitored.

Other investigations in the program are concerned with BG-4, BG-5, and BG-6 and the trench areas, particularly trench 7. Usually the trench samples (water) contain higher concentrations of radionuclides than do any of the burial ground samples; tritium is dominant and may be present in amounts as large as 10^5 pCi/ml in some samples. Indeed, many of the trench samples are too high in radioactivity to be analyzed in the low-level radiochemical facilities, and these are routed to the intermediate-level facilities for analysis. *(T. G. Scott, G. I. Gleason,[2] P. S. Gouge, C. C. Granger, C. V. Holmes, W. C. Massey, N. A. Teasley, A. J. Weinberger)*

Progress in the Low-Level Nuclear Measurements Laboratory

Two additional 20% Ge(Li) detectors were purchased for gamma spectroscopy in the Low-Level Nuclear Measurements Laboratory, located in Building 4500S, Room G-49. With three Ge(Li) systems in operation, sample throughput has been greatly increased. Efficiency calibration of these detectors is essentially complete, so that absolute activity can be reported on a variety of sample configurations, such as Marinelli beakers, petri dishes, and filters.

The two new detectors are equipped with heavy, Applied Physical Technology (APT) shields and exhibit a markedly reduced background. Detection limits are significantly lower and can be as low as 5 dis/min for many radionuclides. Area monitor samples for ^{131}I release have been moved from NaI to the Ge(Li) systems for measurement. A 50-min count has a medium detectable activity of 6 dis/min with no interference from ^{222}Rn, ^{75}Se, and other radionuclides, which are likely to be adsorbed on the charcoal filters. Sample results are also immediately available, since computer analysis is not required.

The ND 6603 data acquisition system purchased in 1978 has taken over the work load formerly carried out by the ND 3300. Sufficient memory has been added to allow data to be accumulated from as many as 16 ADCs. At present, it is used with inputs from the three Ge(Li) gamma detectors and five surface-barrier alpha detectors. Plans are to add four additional alpha detectors and three NaI scintillation detectors. The ND 6603 can output photopeak information, which can be used for hand data reduction when speed is essential. However, gamma spectra taken with the ND 6603 are routinely transferred to magnetic tape and taken to the ND 6620 system in Building 3019 for processing. Thus, there is a need to provide for on-line data reduction capability in the Low-Level Nuclear Measurements Laboratory. *(G. I. Gleason,[2] N. A. Teasley, S. A. Reynolds)*

Analysis of ^{99}Tc in Environmental Materials

Interest in ^{99}Tc continues to grow, and the number of requests for the determinations of extremely low levels of this radionuclide in environmental materials, particularly soil, vegetation, and water, has increased during the past year. To meet these demands, we have made a concerted effort to improve methodology and to lower sensitivity for determining technitium.

A decided improvement in the method of analyzing soil has been gained by adopting an extraction procedure that was developed by E. A. Bondietti of the Environmental Sciences Division. The main feature of this procedure is the use of NaClO, either cold or at elevated temperatures, plus H_2O_2 as a medium for extracting technetium from soil. Following the extraction, slightly modified radiochemical techniques are used to complete the analysis. By utilizing this combination of techniques, we are now able to analyze 100-g samples; this is approximately four times the weight of sample that was previously analyzed and affords an increase in sensitivity in the analysis.

Our final measurements of ^{99}Tc are presently made by low-level beta counting, which gives a medium detection limit of approximately 10 pCi or 0.6 ng. Beta counting has been inadequate in many cases because of limited sensitivity and lack of specificity of the counting technique. Therefore, we are collaborating with the Mass and Emission Spectrometry Section to utilize isotope dilution mass spectrometry (IDMS) as a final measurement technique for determining low levels of ^{99}Tc. Of course, chemical separations will be required on environmental materials prior to mass spectrometric analysis.

In the determination of ^{99}Tc by the IDMS technique, long-lived ^{97}Tc ($T_{1/2}$, 2.6×10^6 years) is needed for isotopic spikes. Several groups in the Analytical Chemistry Division have collaborated in the preparation of a ^{97}Tc product. Isotopically enriched ^{96}Ru (25 mg) was irradiated for 20 d in the HFIR at a neutron flux of 6×10^{14} neutrons cm^{-2}s^{-1} to produce an estimated 7 μg of ^{97}Tc. Half of the ^{96}Ru target material was chemically processed by the Operations Division to recover the technetium isotopes, and the other half was retained for future use. The total technetium yield from the processed target was 1.6 μg, with an isotopic composition of 80% ^{97}Tc, 20% ^{98}Tc, and 0.17% ^{99}Tc. This is sufficient ^{97}Tc to allow for the analysis of several hundred samples by IDMS, when using approximately 1 ng of ^{97}Tc per analysis.

In the production of ^{97}Tc from the ^{96}Ru target, we were surprised to find the high ^{98}Tc and ^{99}Tc content of the product. These technitium isotopes are formed by successive neutron captures on ^{97}Tc. Cross-section data are not now available for these reactions, but our findings suggest that the cross sections are high. We are making arrangements to irradiate a small portion of the technetium product under well-defined flux conditions so as to accurately determine the cross sections of the ^{97}Tc(n,γ)^{98}Tc and ^{98}Tc(n,γ)^{99}Tc reactions. The cross sections will be based on mass spectrometric determinations of the isotopic ratios before and after irradiation. The cross section of the ^{98}Tc(n,γ)^{99m}Tc reaction will also be determined by a separate irradiation and gamma-ray spectrometric determination of ^{99m}Tc. These data will allow future productions of ^{97}Tc to be made under conditions that will maximize ^{97}Tc and minimize ^{99}Tc in the product. *(T. G. Scott, J. F. Emery, S. A. Reynolds, R. L. Welker,*[4] *C. V. Holmes)*

Nonroutine Radioanalyses That Require Special Techniques

Samples of coal, coal ash, fly ash, and condensed stack vapors are products of an experiment to determine the ultimate fate of radionuclides of the natural chains during the operations of coal-fired steam plants. Several of these materials are highly refractory and require particular attention when analyzed for ^{210}Po and ^{210}Pb. Ordinary ashing procedures are impractical for these determinations because of the volatility of these elements. Consequently, either wet ashing or low-temperature ashing is necessary for preparing materials for the radioanalysis. Following total dissolution of the ash, ^{210}Po is purified by the usual chemistry and then deposited on silver by spontaneous deposition. Lead-210 is determined indirectly by assuming equilibrium, separating out the ^{210}Bi daughter, and measuring the ^{210}Bi by low-background beta counting. Decay counting is used to verify the purity of ^{210}Bi.

Mineral-wool insulation samples required analyses for uranium, thorium, and ^{226}Ra. The insulation is made from slag of a coal-fired power plant, and there was concern as to the content of natural radioactivities, particularly ^{226}Ra, the parent of ^{222}Rn, which would be available as a gas and be inhaled. Nondestructive methods were adequate to make the determinations. Neutron activation was used for thorium and uranium determination, and gamma-ray spectrometry was used for the determination of ^{226}Ra by measuring the amount of ^{214}Bi and ^{214}Pb daughters.

Filter samples that were submitted by the Health and Safety Research Division required ^{226}Ra, ^{210}Pb, ^{230}Th, ^{238}U, ^{227}Ac, and ^{231}Pa analysis. Because these were single and unique samples, all of the above nuclides needed to be separated by sequential separations; however, ^{231}Pa is one radionuclide that is rarely determined in our lab, and it was necessary to subsample the dissolved filters and hold a portion for the ^{231}Pa analysis, pending the development of a procedure. The determination of ^{227}Ac was accomplished by assuming secular equilibrium and measuring the ^{227}Th daughter by alpha spectrometry.

Special handling and mounting techniques were used in determining the rate of emerging alpha particles from samples of Al_2O_3, silicon, and lead and of aluminum disks. Most of these were high-purity materials that are used as components of advanced memory circuits. Traces of natural activities (uranium and thorium and their daughters) were the contaminants responsible for alpha emissions. Long count times (typically 4300 min), with disposable ZnS(Ag) phosphors, were required to acquire satisfactory sensitivities. *(T. G. Scott, G. I. Gleason,*[2] *P. S. Gouge, C. C. Granger, C. V. Holmes, W. C. Massey, N. A. Teasley, A. J. Weinberger)*

Developments in Low-Level Radiochemical Analysis

The Low-Level Nuclear Measurements Laboratory is frequently requested to analyze samples for which no specific calibration exists. A method is under development that would enable a reasonable estimate of detection efficiency for such samples based on the dimensions and density of the sample with reference to a master calibration curve (prepared from NBS point sources). The method involves the use of a point source to establish detector response as a function of both vertical and lateral displacement from the center of the detector face, where the relative efficiency is maximal and is taken as unity. From these data, an estimate of the relative efficiency of an extended source can be made. Application of this technique to various calibrated sample geometries has produced acceptable results.

SPECIAL PROJECTS

Cerenkov Counting of Low-Level Beta Radioactivity

Cerenkov counting[5] involves the measurement of light photons emitted when an electron traverses a transparent medium at a velocity greater than that of light. Only electrons with energies greater than 0.26 MeV can be detected in dilute aqueous solutions. The applicability of the technique to measurement of low-level beta radioactivity was investigated, with particular reference to the ^{90}Y daughter of ^{90}Sr. Initial experimental studies were made with commercial liquid scintillation counting instrumentation. Efficiencies and backgrounds were determined for various types of sample vials, after optimizing gain and pulse height for the counting of ^{90}Y. Polyethylene vials have been found to be better than glass with regard to efficiency and background.

For low-level analyses, the blank is of special significance because of its effect on the sensitivity of the analysis. We have observed that blanks are about 5 cpm with inactive solutions in the scintillation counter, and that the blank is lowered markedly by adding a quenching agent to the solution. When an opaque suspension of ink was used, the value of the blank fell to about 1 cpm. It is concluded from these observations that electronic noise is a minor contributor to the blank, but that Cerenkov light, produced in system components by beta, gamma, and cosmic radiation, increases the background count.

With present settings of voltage, gain, and discrimination, efficiencies for nuclides of interest are as follows: ^{90}Y, 42%; ^{90}Sr, $\leq 0.4\%$; ^{85}Sr, $\leq 0.04\%$; ^{137}Cs, 1.4%; and ^{60}Co, 3.3%. The efficiency for ^{222}Rn daughters is about 22%, but most of this potential interference can be removed by sweeping radon from a water sample with air and allowing about 2 h for decay of radon daughters before counting. Minimum detectable activity of ^{90}Y for a 100-min count is calculated to be 1.5 dis/min.

The usefulness of Cerenkov counting for direct screening was shown by counting 20-ml aliquots of 11 water samples and then comparing results expressed as ^{90}Y with radiochemical determinations. Results agreed on nine of the 11, and the remaining two were found to contain substantial concentrations of ^{137}Cs and ^{60}Co. Early results were reported in a paper at the recent International Conference on Liquid Scintillation Counting and will appear in the proceedings of the meeting.

Chemical separations are necessary in many cases to concentrate strontium and yttrium from large aqueous volumes, to remove interfering radionuclides, or to eliminate colored substances that cause quenching. Because of the general insensitivity of the technique to chemical composition of the solution used for counting and the discrimination against low-energy beta radiation, simple separation schemes can be used with increased speed and safety as compared with conventional methods.

Concentration is effected by adsorption on a cation-resin column from solution at pH = 1 (usual storage condition). Elution is done with 5 M NH_4Cl; strontium and yttrium are then coprecipitated with CaC_2O_4, which is dissolved in HCl and placed in a vial for counting. Recoveries in the column separation are 90% or better for volumes as large as 1 liter, and the oxalate precipitation achieves essentially quantitative recovery from samples of water or soil leach solutions. For ruthenium, the decontamination factor of the column separation is about 4, while decontamination factors in the oxalate precipitation for cesium, ruthenium, and cobalt are about 300, 10 to 30, and 10 to 20, respectively.

It is expected that Cerenkov counting will be used for analysis of routine samples in the near future, employing both direct screening and counting after separation. Full implementation, however, will require the acquisition of a liquid scintillation counter with high sample throughput. *(S. A. Reynolds, J. S. Eldridge)*

Geochemistry of Achondritic Meteorites: Gamma-Ray Studies

A high-sensitivity, low-background, gamma-ray spectrometer containing two 23-cm × 13-cm thallium-activated, sodium iodide detectors was used to measure long-lived primordial and cosmogenic radioactivity in a suite of achondritic meteorites. Potassium, thorium, uranium, and ^{26}Al abundances were established for 16 brecciated eucrites, two unbrecciated eucrites, a nakhlite, a chassignite, and a unique meteorite from Antarctica by nondestructive counting techniques. In several cases, multiple samples of the same meteorite fall were examined. Concentrations ranged from 79.8 ppm to 1150 ppm for potassium, 55.6 ppb to 663 ppb for thorium, 18.1 ppb to 190 ppb for uranium, and 45.0 dis min^{-1} kg^{-1} to 99.0 dis min^{-1} kg^{-1} for ^{26}Al. In addition, a ^{137}Cs concentration of 264 dis min^{-1} kg^{-1} was observed in the Allan Hills 77005, 9 specimen.

Standards were prepared by dispersing small quantities of solids containing potassium, thorium, uranium, ^{26}Al, and ^{137}Cs into finely divided iron powder. These mixtures were placed in polyethylene bags, which were then counted in the same geometries as those of the corresponding meteorite specimens. Counting times for the standards varied from approximately 1 to 3 h, while those for the achondrites ranged from about 5 to 15 d. The densities of the meteorite specimens were determined by the use of water phantoms constructed from aluminum foil that was coated with epoxy resin. In addition, documented specimens weights were verified.

Data reduction was accomplished with the aid of programs MOON and ALPHA-M. Experimental data were transferred from the memory of a multichannel analyzer unit to paper tapes and then were preprocessed through program MOON. Data cards returned as part of the output package from program MOON were sorted and subsequently used in ALPHA-M, a least-squares fitting program designed for the analysis of gamma-ray spectra.

Correlations between potassium (a volatile element) and thorium and uranium (both refractory elements) were made in relation to current models of meteorite genesis, based on fractional crystallization and partial melting processes. Cumulate species, the first achondrites to form in underground magma chambers, exhibited decreased abundances of these elements compared to noncumulate species. In addition to experimentally determined values, theoretical abundances of ^{26}Al were calculated for each meteorite specimen, based on target element concentrations. Anomalously low experimental-to-calculated ^{26}Al/^{26}Al ratios were observed for many of the achondrites. Based on ^{26}Al measurements, an upper limit of 4.94 × 10^5 years was suggested for the terrestrial age of the Allan Hills 77005 achondrite from Antarctica. This study was submitted to the University of Tennessee as a doctoral dissertation in August 1979. *(R. A. Muntean,*[*] *G. D. O'Kelley,*[†] *J. S. Eldridge)*

Radionuclide Transport: Characterization of Species and Sources at a Solid Waste Disposal Site

A collaborative project designed to determine radionuclide transport mechanisms was conducted with the Environmental Sciences Division at a 2.8-ha (7-acre) storage site for low-level contaminated equipment. An additional purpose of the study was to characterize the extent of surface contamination as to radionuclide types and concentration so that economical cleanup procedures could be employed when removal of the contaminated equipment was completed.

A 30-m sampling grid was laid out on the site and 38-cm core samples were taken at each grid intersection. The core sections were segmented into three portions: 0 to 13, 13 to 26, and 26 to 38 cm. Each of these three depth horizons was analyzed for radionuclide content after drying, homogenizing, and pulverizing. High-resolution gamma-ray spectrometry was used to determine the type and concentration of gamma-emitting radionuclides, and specific radiochemical separations were used for determining ^{90}Sr and some alpha-emitters.

The surface samples (0 to 13 cm) at all the 30 grid locations contained detectable quantities of the gamma-ray emitters ^{137}Cs and ^{60}Co. Only six of the surface samples contained ^{137}Cs concentrations exceeding 100 pCi/g, with a maximum value in one core of 880 pCi/g. The bottom segment of each core contained very small quantities of radionuclides. Specific radiochemical separations were performed for ^{90}Sr, ^{239}Pu, and ^{241}Am in many of these cores. Incomplete results for ^{90}Sr show a range of surface concentrations from 0.3 to 200 pCi/g. In general, the decrease of ^{90}Sr concentration with depth was not nearly as dramatic as that for ^{137}Cs; in fact, the ^{90}Sr concentration in the bottom segment (26 to 38 cm) of one core was 50% greater than that in the top segment (0 to 13 cm) for that core.

Concentrations of ^{239}Pu (partial results) ranged from the detection limit to a few hundred picocuries per gram for the surface. Americium-241 was present in some surface samples to a maximum of 40 pCi/g. Both of the transuranic nuclides exhibited decreases of concentration with depth similar to that shown by ^{137}Cs. That the mobility of ^{90}Sr was greater than that of the other nuclides studied was readily apparent. Subsequent field measurements of the site with a portable gamma-ray spectrometer led to an identification of possible sources for the small surface contamination.

Iodine-129 was measured in three water samples collected in this study. Values ranged from 2.4 to 8.5 μg of ^{129}I per liter for the three solutions. The ^{129}I determinations were performed by ion exchange concentration, followed by neutron irradiation, to produce ^{130}I. From the nature of the solution, calculations based on solubility product principles verified the experimentally determined concentrations of this long-lived fission product.

Surface drainage pathways from the site were sampled to determine the migration of the contaminating radionuclides. Mineral separation of selected core samples was made to determine the matrix soil type responsible for the movement of ^{137}Cs. *(J. S. Eldridge, T. G. Scott, H. A. Parker, A. M. Stueber,[8] T. W. Oakes[9])*

Investigation of ^{137}Cs, ^{60}Co, and ^{90}Sr Concentrations in Water and Sediment as a Function of Flow in White Oak Creek

White Oak Creek tributary surface streams flow through the Oak Ridge reservation and receive treated low-level radioactive liquid waste, which originates from various Laboratory operations. The streams receive additional low-level liquid waste by seepage of radioactive materials from solid-waste burial grounds, hydrofracture sites, and intermediate-level liquid waste burial sites. An important consideration in the measurement of radionuclide discharges is the amount that is transported in the water and in sediment. Because ^{137}Cs, ^{60}Co, and ^{90}Sr may either become absorbed by stream sediments or remain in solution, the percentage of these nuclides associated with the water and sediment as a function of flow is being investigated at periods of high flow conditions.

Sample collection is initiated at times of heavy rains when the flow reaches 800–1000 liters/s. Samples are collected at half-hour intervals, and then hourly collections are made as the study progresses. The water samples are filtered through 1 μm Millipore filters as soon as possible after collection. The filtrate is acidified with 10 ml of concentrated hydrochloric acid, and the filters containing the sediment are dried and weighed to determine the total sediment transport. High-resolution gamma-ray spectroscopy is used to determine the radionuclide content of the solution and of sediment fractions. Radiochemical separations are performed to determine the ^{90}Sr content of each solution and sediment sample.

In a recent two-day study, sufficient samples were taken to characterize the system thoroughly during high flow conditions. Figure 5.1 shows the water flow pattern during the March 3 study starting with a flow of 1400 liters/s, reaching a crest of 8000 liters/s after 5 or 6 h, and then tapering off to a flow of 1400 liter/s on the second day. Figure 5.2 shows the profile of the solid transfer for the same period. There is a dramatic rise in solid transfer (100 to 700 g/s) occurring during the one-hour span between samples 8 and 10. It is also seen that solids are moving across the dam at 0.8 to 0.9 kg/s at the peak flow period. Figure 5.3 illustrates the temporal variation of

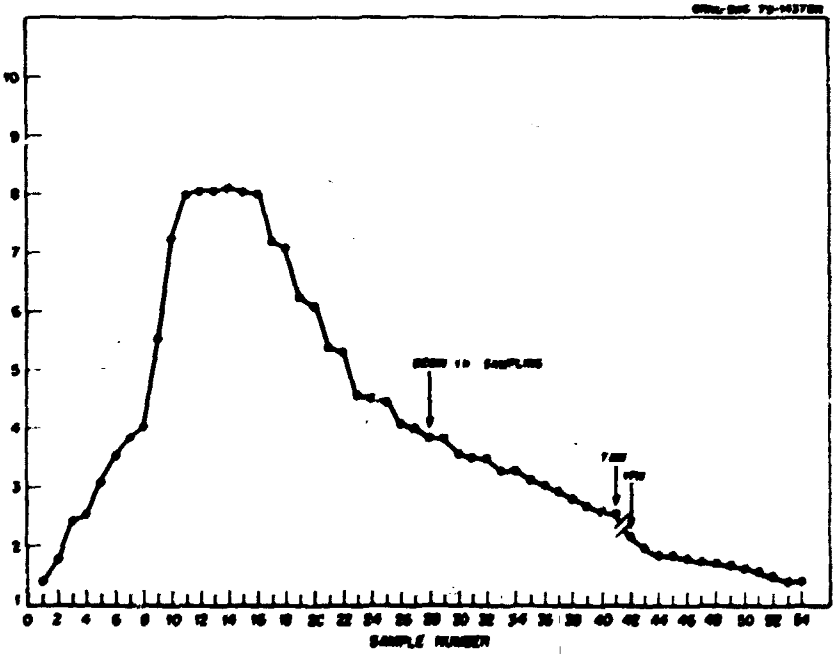

Fig. 5.1. Water flow profile over White Oak Dam during the period 0330 March 4 to 2400 March 5, 1979.

radionuclide transport in sediment. The sediment radioactivity consists predominately of ^{137}Cs, with lesser quantities of ^{60}Co and ^{90}Sr. The ^{137}Cs transport in solids crested at ~8 μCi/s near the flow maximum. However, the ^{137}Cs content per gram of sediment was greatest near the beginning of the experiment when the sediment levels were of the order of 10-12 mg/liter.

The solution transport profile (Fig. 5.4) shows that ^{90}Sr and ^{60}Co are the two major nuclides moving in

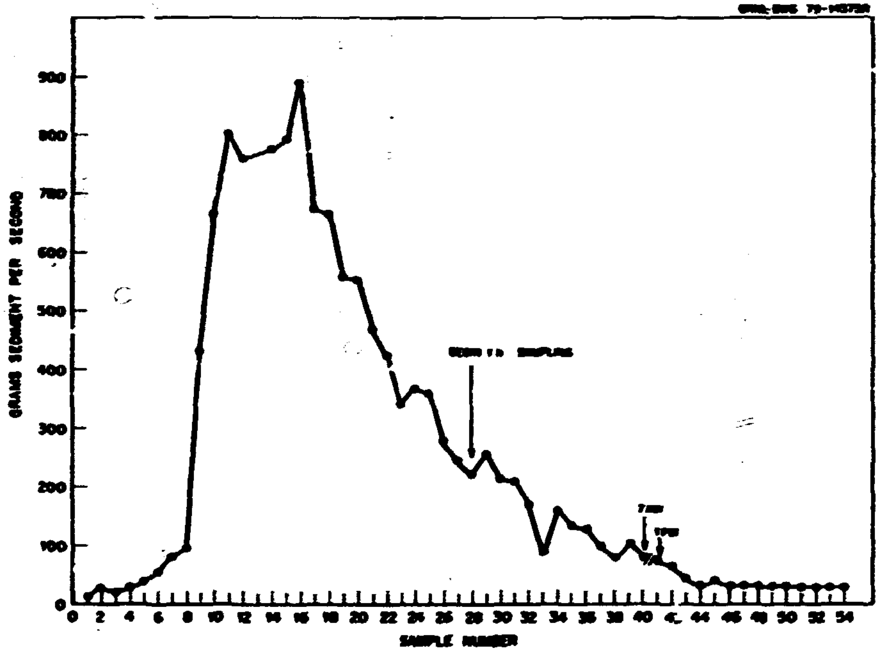

Fig. 5.2. Sediment transfer over White Oak Dam, 0530 March 4 to 2400 March 5, 1979.

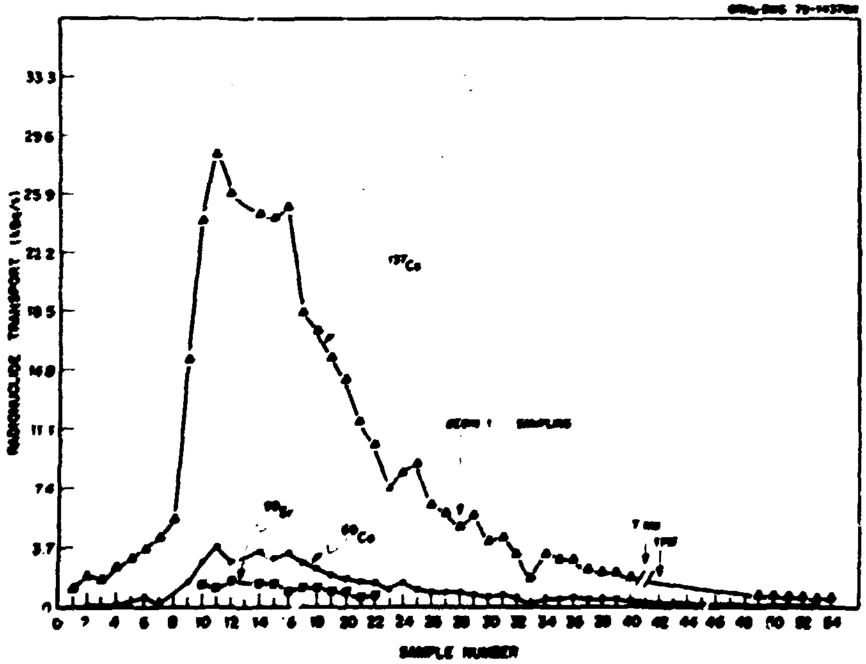

Fig. 5.3. Temporal variation of radionuclide transport in sediments over White Oak Dam, 0330 March 4 to 2400 March 5, 1979.

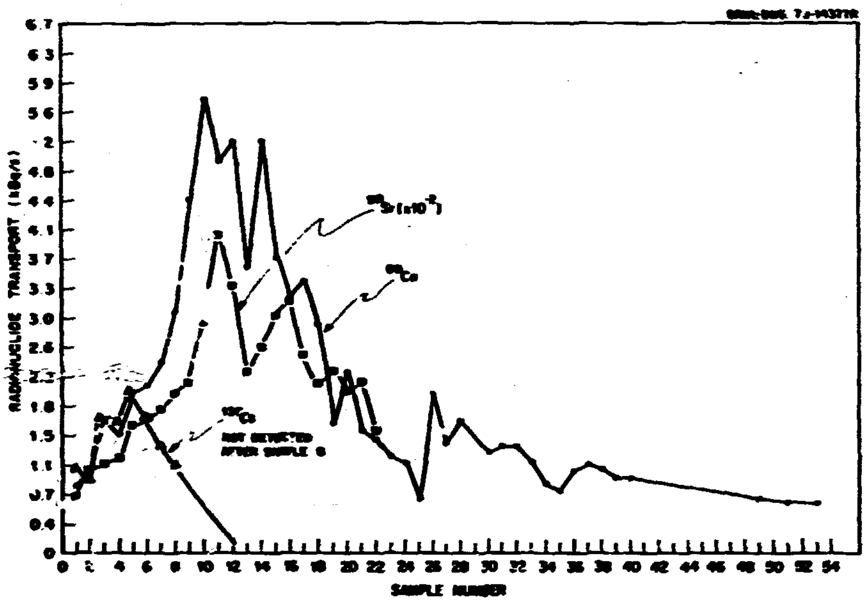

Fig. 5.4. Temporal variation of radionuclide transport in solution over White Oak Dam, 0330 March 4 to 2400 March 5, 1979.

solution across the dam. Note that ^{137}Cs was not detected in solution after the first 4 h and that values plotted for ^{90}Sr are scaled down by 10 (i.e., the maximum point shown for ^{90}Sr at sample number 11 is 1.1 µCi/s.

On the basis of results from the studies of March 3 and 4, it can be shown that ^{137}Cs movement out of the White Oak Creek water system is almost exclusively as a component of sediment; ^{90}Sr moves mainly in solution. Movement of ^{60}Co is seen to be intermediate between the other nuclides (i.e., it moves in both solution and sediment phases). *(J. S. Eldridge, T. G. Scott, T. W. Oakes,[9] K. E. Shank[9])*

Specific Radionuclide Analyses Applied to Air-Monitoring Samples

Specific radionuclide analyses have been applied to air-monitoring samples from three ORNL networks for the past five years. The remote network (8 stations), perimeter network (10 stations), and local network (13 stations) operate on a continuous basis and provide useful indication of atmospheric radioactivity releases from local or distant sites.

Sampling for radioactive aerosols is carried out by passing air continuously through filter papers that are changed weekly. Each paper from every station is evaluated weekly by gross-beta and gross-alpha counting techniques. Composites of collections from each of the three networks over a 13-week period are prepared for specific radionuclide analyses by high-resolution gamma-ray spectroscopy. More frequent specific tests are performed if airborne radioactivity concentrations in the environment are significantly above normal.

On-line computer resolution of the gamma-ray spectroscopic data results in the quantitative estimation of 12 to 14 radionuclides in a composite sample during periods of fresh fallout and for 8 to 10 radionuclides in times when fallout is at a minimum. The gamma-emitting radionuclide present in greatest concentration in the quarterly composite samples is ^{7}Be, which has a half-life of 53 days and is produced by cosmic-ray bombardment of oxygen and nitrogen in the upper atmosphere. The relative constancy of production of ^{7}Be serves as an excellent quality-control measure in air-monitoring procedures. Table 5.3 presents the quarterly composite analysis of ^{7}Be for the years 1975–1978 for the local, perimeter, and remote air-monitoring networks at ORNL.

Detailed examination of Table 5.3 shows an average concentration of ^{7}Be in local air-monitoring composites that is approximately 20% greater than corresponding composites of the other two networks. This effect results from the higher collection efficiency for the local air-monitoring filters, due to a sampling flow rate that is 50% of the perimeter and remote air-monitoring flow rates. An additional effect that arises in ^{7}Be monitoring in all three networks is the 25% increase in ^{7}Be concentrations in the

Table 5.3. Concentration of ^{7}Be in quarterly composite air-monitoring samples, 1975–1978

Units of 10^{-6} pCi/liter

	Quarter			
	1	2	3	4
	Local network			
1975	165	173	150	134
1976	[illegible]	230	181	133
1977	145	193	121	105
1978	117	128	114	91
	Perimeter network			
1975	94	136	105	105
1976	120	180	160	104
1977	127	140	121	101
1978	117	124	106	97
	Remote network			
1975	116	162	104	110
1976	130	162	149	93
1977	132	170	127	99
1978	117	124	102	85

second quarter of all three networks compared with the average concentration of the first and third quarters. In addition, the final quarter of each network exhibits a 20% decrease in ^{7}Be concentration compared to the first- and third-quarter average.

The concentrations of ^{137}Cs, a long-lived component of global fallout, showed variations during the four-year study period from a low of 0.3 × 10^{-6} pCi/liter in the fall of 1975 to a high value of 4.4 × 10^{-6} pCi/liter in the spring of 1978. The gradual increase due to Chinese testing was apparent, and the current values are once again below 1 × 10^{-6} pCi/liter. Variations in concentrations of ^{144}Ce, an intermediate half-life fallout nuclide, showed wider ranges from 1 × 10^{-6} to 40 × 10^{-6} pCi/liter, with the maximum concentrations occurring in the spring of 1977. Data for approximately ten specific radionuclides are available for the four-year study period in this program.

The air-monitoring networks at ORNL serve as useful fallout monitoring devices and show the effects of local releases to the environment. Airborne concentrations tabulated in this four-year study are at least a thousand times less than the applicable DOE concentration guides for radionuclides detected. *(J. S. Eldridge, T. W. Oakes, K. E. Shank)*

Gamma-Ray Spectrometry for Environmental Monitoring and Surveillance: Animal Studies

Road-killed deer on the Oak Ridge reservation have served as a useful biological monitoring system for various gamma-emitting radionuclides that are important in assessing local effects on man's radiation dose.[10] Because these samples are available at unpredictable times, it is desirable to minimize sample preparation procedures. Accordingly, we have modified our techniques to allow the use of fresh tissue that has been suitably homogenized.

At autopsy, a sufficient quantity of muscle and liver tissue is taken to yield a sample volume of approximately 1 liter. The tissue is placed in a heavy-duty blender and homogenized. A suitable quantity of the homogenized tissue is then transferred to a Marinelli beaker for counting in the high-resolution spectrometer system for a period of at least 50,000 s. With such a geometry and counting interval, we can achieve a minimum detection limit of 1 to 2 pCi/kg for ^{137}Cs in fresh tissue. This sensitivity is more than adequate since global fallout exceeds these values by an order of magnitude. Results for the analysis of deer killed during the second half of 1978 and early 1979 are listed in Table 5.4; the estimate of overall inaccuracy is ±10 to 15% and units are expressed as picocuries per kilogram (fresh weight).

Table 5.4. Radionuclide concentrations in road-killed deer

Sample	Sex	Organ	^{137}Cs (pCi/kg)	^{40}K (pCi/kg)
D8-4	F	Liver	10.2	1290
D10-5	F	Liver	50.9	1650
D11-10[a]	M	Liver	27.3	1530
D11-12	M	Liver	11.9	2190
D11-12	M	Heart	24.7	1380

[a] This animal contained 21 pCi/kg ^{65}Zn in addition to the nuclides listed.

Muscle content of ^{137}Cs yields information concerning dose to the animal over relatively long periods of time, whereas liver analyses show the effect of more recent exposures. We plan to expand the sampling regime to include the rumen as an additional sample, which will be useful in assessing the animal's most recent dose encounter. *(J. S. Eldridge, W. C. Massey, J. M. Mahathy, T. W. Oakes)*

Alpha Spectrometry of Unusual Samples

A silicon detector of 20-cm^2 area has been in use for alpha spectrometry for more than four years. Its output now feeds the ND 6603 analyzer and covers a range of 1 to 10 MeV. System advantages include the wide energy range and the possibility of studying spectra of large-area samples. Many spectra have been taken which were related to the search for unknown alpha emitters[11] by R. V. Gentry of the Chemistry Division. Various natural radionuclides were identified, sometimes in unusual mixtures requiring interpretation based on the sample histories.

Metallic lead disks were examined for emergent alpha of ^{210}Po, daughter of ^{210}Pb, present at various levels. Spectra had the degraded appearance characteristic of alpha radiation originating throughout a solid. After cleaning the lead samples with a CH_3COOH-H_2O_2 mixture, we noted sharp peaks at the ^{210}Po energy, indicating thin deposits. One of these deposits was removed by abrasion, and only the degraded spectrum remained. It was surmised that a thin layer containing polonium and lead was dissolved and that the polonium deposited in part on the fresh lead surface.

In another project, replicate gross-alpha determinations on water samples had variations, which could be interpreted as indicative of the presence of particles carrying the alpha activity (predominantly ^{244}Cm). Data on two of the replicate plates demonstrated that the higher one had a degraded spectrum, while the lower had a spectrum of good resolution, thus neatly verifying the postulate of particulate activity. *(S. A. Reynolds, J. F. Emery)*

Quality Assurance for the Special Projects Group

Low-level gamma-ray spectrometric measurements in Laboratory G-4 are performed with a high-resolution Ge(Li) detector system coupled to an on-line computer-based analyzer. Data reduction is accomplished by means of system software for some applications and by means of an IBM 360 program (MONSTR) for most sample types. System calibrations are performed with standard reference materials from the NBS or with analyzed standards from the New Brunswick Laboratory (NBL) in the case of uranium and thorium analyses.

Quality control of the spectrometer system in the G-4 lab is accomplished on a regular basis by use of a scheme that checks the reliability of the various steps involved in a complete analysis. A sample of NBL uranium standard 42-4 containing 70.0 g of 0.52% uranium in dunite is analyzed with the spectrometer at least one time for each group of 30 samples collected on the compatible magnetic tape system. The magnetic tape containing 30 spectra is processed at the central computer facility with program MONSTR. Results from this program are produced by a technique of peak search and nuclide identification with values calculated in units of picocuries per gram. Because the major gamma-ray lines in a natural uranium source arise from radium daughters, the quality control values for ^{226}Ra are tabulated for complete assurance testing from the detector performance all the way through the procedure to the control of the computer programs.

Three procedures—"Specific Radionuclide Analyses Applied to Air-Monitoring Samples," "Semiannual Grass Sample Analysis-High-Resolution Gamma-Ray Spectroscopy Method," and "Semiannual Soil Sample Analysis-High-Resolution Gamma-Ray Spectroscopic Method"—were written for the ORNL Environmental Surveillance and Evaluation Program.

A 2π gas-flow proportional counter has been calibrated with NBS reference materials and is used for nonroutine alpha measurements and preparation of secondary standards for the section. A paper, "Quality Assurance Applied to Environmental Radiological Surveillance," by T. W. Oakes, K. E. Shank, and J. S. Eldridge, has been accepted for publication in the journal *Nuclear Safety*. *(S. A. Reynolds, J. S. Eldridge)*

REFERENCES

1. Sabbatical leave from Denison University, Granville, Ohio.

2. On loan from Oak Ridge Associated Universities.

3. A. M. Stueber, D. A. Webster, I. L. Munro, N. D. Farrow, and T. G. Scott, *An Investigation of Radionuclide Release from Solid Waste Burial Area 3, Oak Ridge National Laboratory*, ORNL/TM, in review.

4. Mass and Emission Spectrometry Section.

5. C. T. Peng, "Liquid Scintillation and Cerenkov Counting," pp. 79–149 in *Radiochemical Methods in Analysis*, D. I. Coomber, ed., Plenum Press, New York, 1975.

6. Tennessee Valley Authority, Muscle Shoals, Alabama.

7. Chemistry Division.

8. Environmental Sciences Division, presently at Louisiana State University.

9. 9. Industrial Safety and Applied Health Physics Division.

10. J. S. Eldridge, W. C. Massey, and T. W. Oakes, "Low-Level Gamma-Ray Spectrometry Development for Environmental Monitoring," *Anal. Chem. Div. Annu. Prog. Rep. Dec. 31, 1978*, ORNL-5518, pp. 90–91.

11. M. A. K. Lodhi (ed.), *Superheavy Elements*, pp. 123–213, Pergamon Press, New York, 1978.

6. Quality Assurance, Safety, and Tabulation of Analyses

L. T. Corbin, Quality Assurance Officer
G. R. Wilson, Assistant Quality Assurance Officer
G. R. Wilson, Safety and Radiation Control Officer

QUALITY ASSURANCE

The Quality Assurance (QA) Program for the service groups of the Analytical Chemistry Division is now a part of the Data Management System (DMS). The QA portion of the DMS aids management in verifying the accuracy of analytical tests performed on customer samples. Analyses are performed simultaneously on a customer sample and a control sample. The test results of the control samples, the determination method used, the technician's initials, and other identifying information are entered into the computer by running the TECHN (or T) program. The QA officer enters the known values of all control samples into the system by either running the CNTLIN interactive program or by submitting control data sheets to be keypunched and processed in batch mode. The MANINQ program is used by the QA officer to generate daily, monthly, or quarterly statistical reports and graphs showing the comparison of technician test results and actual known values. The SUPV (or S) program is used daily by the lab supervisors for information on which test results exceeded 1.5 times the limit of error. The system accumulates data on a quarterly basis, and, at the end of each quarter, all data files are removed and stored on a computer-readable media.

The quality of the division's work is also being checked by having customers submit simulated samples prepared by the assistant QA officer but bottled and labeled by the customer.

Table 6.1 shows the quality level for each of the service laboratories and gives a comparison of results. Lists of the different control programs and the number of results reported for each program are given in Table 6.2.

Table 6.1. Distribution by laboratory of control tests for October 1978–September 1979

Laboratory	Number of control results		Quality level[a] (%)	
	Total	Outside fixed limits	1978	1979
General Analytical	1118	41	94.60	96.33
Environmental Analysis	784	46	96.04	94.13
Radioactive Materials	425	42	95.24	90.12
Transuranium	444	11	95.21	97.52
Total	2771	140	95.16	94.95

[a] Control results within 2 σ limits.

Table 6.2. Distribution of control results (by method) for October 1978–September 1979

Method	Constituent	Number of programs	Number of results	Total for method
Atomic absorption spectrometry	Aluminum	1	59	
	Calcium	2	84	
	Cadmium	2	1	
	Chromium	1	30	
	Copper	2	20	
	Iron	1	79	
	Lithium	2	17	
	Magnesium	2	59	
	Manganese	1	[illegible]	
	Nickel	1	26	
	Potassium	2	46	
	Ruthenium	2	86	
	Sodium	2	85	
	Zinc	2	8	604
Colorimetry	Chloride	1	57	
	Molybdenum	1	97	
	Nitrate	1	19	
	Nitrogen	2	144	
	Phosphorus	1	62	
	Sulfate	2	104	
	Thorium	2	71	
	Uranium (NH_4SCN)	3	152	
	Uranium (DBM)	1	100	
	Zirconium	1	14	820
Coulometry	Uranium	2	54	54
Fluorometry	Uranium	2	357	357
Gravimetry	Carbon (Leco)	1	144	
	Carbon (train)	1	10	
	Hydrogen (carbon train)	1	10	164
Infrared spectrometry	Carbon	1	62	62
Ion selective electrode	Fluoride	1	56	56
Volumetry	Acid	3	260	
	Nitrate	1	32	
	Sulfur	1	68	
	Thorium	3	112	
	Uranium	3	182	654
Total		58		2771

SAFETY

During the past year, the Analytical Chemistry Division had one recordable injury (the same as last year) and three first-aid cases as compared to seven cases last year; all were cuts or burns. The Safety Committee has inspected the division each quarter, accompanied part of the time by the Division Director. All of the division attended an environmental awareness seminar, and some members attended the oil disposal workshop, the chemical disposal workshop, and defensive driving classes. Two copies of *The Laboratory Safety Deskbook*, a guide to Occupational Safety and Health Act standards, have been distributed to each section.

SUMMARY OF ANALYSES RENDERED

Table 6.3 contains a tabulation of support analyses performed by the various laboratories and/or groups within the division during this reporting period.

Table 6.3. Summary of analytical work

Organization	Mass Spectrometry	General Analytical	Transuranium Analysis	Radioactive Materials	Physicochemical	Nuclear and Radiochemical Analysis	Total
	Number of results reported by laboratory						
ORNL divisions							
Analytical Chemistry	1,272	1,981	8	57	104	2,306	5,728
Biology	40						40
Central Management[a]					34	123	157
Chemical Technology	24,958	16,367	42,562	15,400	1,960	12,242	113,489
Chemistry	3,120	2,435	83	342	1,225	1,067	8,272
Engineering		127					127
Engineering Physics	235				163		398
Engineering Technology	641	4,451		93	354	239	5,778
Environmental Sciences	173	19,052		48	636	6,657	26,566
Fusion Energy	147						147
Health	1,255				5		1,260
Health and Safety Research	166					1,103	1,269
Industrial Safety and Applied Health Physics		9,546	8		50	10,989	20,593
Instrumentation and Controls	287	160		42			489
Metals and Ceramics	13,169	4,621	6	549	1,224	154	19,723
Operations	1,204	1,716	8,505	693	115	9,939	22,172
Physics	131			84	30	1	246
Plant and Equipment	392	76			602		1,070
Quality Assurance and Inspection	27						27
Solid State	1,764	192	30	25	341	714	3,066
Others							
Protective Coating Testing				1,355		1,520	2,875
NURE[b]						17,528	17,528
K-25 and Y-12	1,058					24	1,082
Miscellaneous	13,973			158	3	309	14,443
Total	64,012	60,724	51,202	18,846	6,846	64,915	266,545

[a] Not a division.

[b] National Uranium Resource Evaluation.

7. Supplementary Activities

The division continues to maintain liaison with the academic community through the assistance of its Advisory Committee and consultants. We also make facilities and supervision available for student and faculty research and training programs.

ADVISORY COMMITTEE

This year the division Advisory Committee was composed of

P. F. Kane, Director of Materials Characterization Laboratory, Texas Instruments, Inc., P.O. Box 5936, MS 147, Dallas, Texas,
L. L. Lewis, Head, Analytical Chemistry Department, Research Laboratories, General Motors Corporation, 12 Mile, Mound Roads, Warren, Michigan,
H. L. Pardue, Chemistry Department, Purdue University, West Lafayette, Indiana, and
A. G. Sharkey, Acting Deputy Director. Pittsburgh Energy Technology Center, Department of Energy, 4800 Forbes Avenue, Pittsburgh, Pennsylvania.

CONSULTANTS

A. E. Cameron advises the Mass and Emission Spectrometry Section of the division.

M. T. Kelley advises the Analytical Methodology Section, with particular emphasis on computer applications.

The following specialists were brought to ORNL on short-term consulting bases this past year as part of our Seminar Program. Details of seminars are listed in Chap. 8.

E. S. Etz, National Bureau of Standards, Washington, D.C.,
S. T. Cram, Varian Instrument Division, Walnut Creek, California,
M. L. Gross, University of Nebraska, Lincoln, Nebraska,
J. Stöhr, Stanford Synchrotron Radiation Laboratory, Stanford, California,
G. Horlick, University of Alberta, Canada,
D. J. Swaine, Fuel Geoscience Unit, Australia,
F. E. Lytle, Purdue University, West Lafayette, Indiana,
R. G. Cooks, Purdue University, West Lafayette, Indiana,
D. N. Hume, Massachusetts Institute of Technology, Cambridge, Massachusetts,
R. Sievers, University of Colorado, Boulder, Colorado,
J. I. Trombka, NASA-Goddard Space Flight Center, Greenbelt, Missouri.

EDUCATION ACTIVITIES

Two staff members earned degrees from the University of Tennessee during this period:

D. L. Donohue was awarded the Ph.D. by the University of Tennessee, Knoxville. His thesis dealt with channel electron multiplier array detection of spark source mass spectrometry signals. J. A. Carter served on his doctoral research committee, which was chaired by G. Mamantov.

H. Simmons earned the B.A. degree in Business Administration from the University of Tennessee, Knoxville, with a major in economics.

PARTICIPATION IN ORNL IN-HOURS PROGRAM

The following divisional people completed courses during the 1979 winter term of the Continuing Education Program for Scientific and Technical Personnel:

C-200A. Organic Chemistry Enricher I: C. S. MacDougall.

E-500A. Survey of Microprocessors and Microcomputers: A. R. Crook.

M-301A. Introduction to the DECsystem-10: R. W. Holmberg.

S-202F. Design and Structure of Technical Writing: J. L. Marley.

S-400A. Searching the Technical Literature: F. L. Layton and J. H. Stewart, Jr.

The following courses were completed during the spring 1979 term:

C-450. The Organic Structure and Reactivity of Coals: C. E. Higgins, W. S. Lyon. and B. A. Tomkins.

M-600C. Practical Statistics I: J. M. Mahathy and T. G. Scott.

Courses completed during the fall 1979 term were:

C-450A. Russian I: C.-h. H[illegible].

IAEA FELLOWSHIP PROGRAM

Belen C. Balboa, Supervising Radiochemist, National Power Corporation, Morong, Bataan, Philippines, was assigned to the division from October 1979 to April 1980. She is working in the Low-Level Radiochemical Analysis Laboratory and in the Radioactive Materials Analytical Laboratory.

GUEST ASSIGNMENTS

Dr. Marie-France Gonnord completed her one-year assignment with M. R. Guerin's section on gas chromatography for chemically characterizing the organic materials produced by and discharged from coal-based technologies. She returned to Ecole Polytechnique, Paris, France.

Mohammad R. Hosseini-Kupaie returned to Iran after receiving training in reactivity of fly ashes as part of his guest assignment.

The University of Tennessee funded a Research Fellow, Sydney White, from Surrey, England, who is involved in spectroelectrochemical studies in molten salts for a four-month period.

Also funded by the University of Tennessee is Vincent E. Norvell, who is working in the Analytical Methodology Section on the study of rapid scan spectrometry.

Geoffrey Gleason, Senior Scientist from ORAU, is on loan to the Analytical Chemistry Division. His assignment is to develop and implement nuclear measurement instrumentation for low-level radiochemical analysis. His specific duties are to setup and calibrate detectors for alpha- and gamma-ray spectrometry and to devise and implement a computer program.

Gail R. Norris is on a one-year sabbatical leave from Denison University. He is assigned to the Nuclear and Radiochemical Analysis Section of the Analytical Chemistry Division and is doing research in the study of trace elements in human lungs.

SUMMER PROGRAM

During the summer, the division was host to representatives of the ORAU Undergraduate Research Program, which has been developed to offer laboratory experience to college students as well as to promising high school graduates. R. W. Holmberg served as "Dean" for these guests during their visit.

V. S. Adams, Carson Newman College, worked in the Bio-Organic Analysis Section on the isolation of mutagenic components from synthetic fuels.

J. R. Kerrigan, University of Pittsburgh, was involved in work related to techniques of thermal and mass spectral analyses in the Analytical Technical Support Section.

P. B. Oldham, Freed-Hardeman College, worked on liquid chromatographic studies in the Bio-Organic Analysis Section.

R. B. Roberson, College of Notre Dame of Maryland, was assigned to the Analytical Technical Support Section to study the chemical kinetic measurements of the decomposition of nitrates.

ORNL CO-OP PROGRAM

Two co-op students were assigned to the division this year:

Darlene L. Moses, Spelman College, Atlanta, Georgia, worked the summer quarter in the Bio-Organic Analysis Section on separations of coal liquids.

Vanessa H. Ostrum, University of Tennessee, worked the fall quarter in the Bio-Organic Analysis Section on the Analysis of benz(*a*)phenanthrene in a variety of sample types.

SPECIAL CITATIONS

A number of Analytical Chemistry Division personnel assisted in work associated with Three Mile Island. The following citations were made by the U.S. Department of Energy:

In appreciation of contributions to analyses in support of emergency efforts following the Three Mile Island accident March 28, 1979:

J. A. Carter
W. H. Christie
L. T. Corbin
J. F. Emery
G. I. Gault
L. R. Hall
L. M. Jenkins
W. R. Laing
L. Landau
E. G. Miller
W. R. Musick
K. J. Northcutt
H. A. Parker
B. Philpot
S. H. Prestwood
J. C. Price
W. D. Shults
H. C. Smith
J. R. Stokely
R. L. Walker

In appreciation of outstanding participation in the successful emergency efforts at the Three Mile Island Nuclear Power Plant following the accident on March 28, 1979:

J. S. Eldridge

23rd ANNUAL ORNL CONFERENCE ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

This year's conference was held at the Riverside Motor Lodge in Gatlinburg, Tennessee, October 9-11, 1979. Attendance was about 200 with 12 exhibitors. Topics covered during the meeting included Radiochemical Separations and Measurements, Radiochemical Determinations and Measurements, On-Line Monitoring and Facilities, Mass Spectrometric Methods, Gamma Spectrometry and Activation Analysis, and Environmental Analysis. Proceedings of the Conference will be published in February 1980.

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A. L. Harrod was General Chairman, W. S. Lyon was Technical Chairman, and Gloria Long and Pat Mullins were Conference Secretaries. Other conference committee members included J. A. Carter, L. T. Corbin, L. M. Jenkins, T. G. Scott, W. D. Shults, and J. R. Stokely.

ADDITIONAL PROFESSIONAL ACTIVITIES

Members of the division continue to serve on professional, civic, and educational boards and committees. These activites are listed below as part of the division's overall outreach.

BALL, F. L.

Secretary: Electron Microscopy Society of America

Representative from EMSA: Section Committee, AAAS Section on Physics (B)

Member: Analytical Chemistry Division Seminar Committee

CARTER, J. A.

Secretary: Subcommittee C-5:05, Analytical Task Group (Reactor Grade Graphite), Committee C-5, Manufacture of Carbon and Graphite Products, ASTM

Member: Committee C-26, Nuclear Fuel Cycle, and C-26:05, Test Methods, Task Group Leader, Micro Analytical Techniques, ASTM

Member: ORNL Management and Supervisory Development Program Advisory Committee

ORNL Personnel Development Chemistry Course

Laboratory Coordinator: ISPO Programs

CATON, J. E.

Consultant: National Cancer Institute

CHRISTIE, W. H.

Member: ACD Seminar Committee
ASTM Committee E-42, Surface Analysis

Invited Speaker: Seventh Canadian Seminar on Surfaces, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, June 11-13, 1979

Session Chairman: Metallurgy Conference on Secondary Ion Mass Spectrometry: Fundamentals and Applications, Takarazuka, Japan, Oct. 23-27, 1979

Combined Techniques, Second Conference on Secondary Ion Mass Spectrometry (SIMSII), Stanford University, Stanford, California, Aug. 27-31, 1979

CLARK, B. R.

Member: Analytical Chemistry Division Seminar Committee

Invited Participant: NIEHS Site Review of Oregon State University Corvallis, Oregon, Nov. 19 21, 1979

CORBIN, L. T.

Fellow: American Society for Testing and Materials

Member: Committee E-10, Nuclear Applications and Measurement of Radiation Effects, ASTM

Subcommittee E-10:01, Fuel Burnup

Subcommittee E-10:02, Radiation-Induced Changes in Metallic Materials

Chairman: Committee C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, ASTM

Coordinator: Analytical Chemistry Division Nontechnical Recruiting

Analytical Chemistry Division Quality Assurance Program

Analytical Chemistry Division Energy Conservation Program

Division Representative: ORNL Job Opportunity System

ORNL Labor Relations

COSTANZO, D. A.

Member: Committee C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, and Subcommittee C-26:05, Methods of Test, ASTM

DYER, F. F.

Lecturer: ORAU Traveling Lecture Program

ELDRIDGE, J. S.

Member: Subcommittee No. 9 (Environmental Radiological Surveillance: Mechanisms for Information Exchange), Health Physics Society

FELDMAN, C.

Fellow: American Society for Testing and Materials

Scientific Editor: *Optics and Spectroscopy* (English translation of Russian journal, *Opika i Spektroskopita*)

Member: Committee E-2 on Emission Spectroscopy, ASTM; Subcommittees on Fundamental Methods, Editorial Practices, and Nomenclature

Member: Atomic Absorption and Emission Spectroscopy Subgroup, Union Carbide Corporation

GUERIN, M. R.

Consultant: National Cancer Institute

Invited Lecturer: BETC Spring Seminar Series, Bartlesville, Oklahoma, May 1979.

Central Research and Development Department, E. I. DuPont de Nemours and Company, Wilmington, Delaware, May 1979

Occupational and Health Control in Fossil Energy Technologies, 1979 National Meeting of the American Chemical Society, Washington, D.C., Sept. 11–14, 1979

Invited Lecturer: Toward a Less Hazardous Cigarette, Cold Spring Harbor Laboratory, Cold Spring Harbor, New York, Oct. 14–16, 1979

Member: EPRI Source Assessment Advisory Subcommittee

HIGGINS, C. E.

Coordinator: Analytical Chemistry Division Affirmative Action Program

HOLMBERG, R. W.

Coordinator: Analytical Chemistry Division University Relations

Analytical Chemistry Division Metrics Conversion

HULETT, L. D.

Invited Speaker: Univ. Nac. Auton. de Mexico, Inst. de Fis., Nov. 13–14, 1979

JENKINS, R. A.

Consultant: National Cancer Institute

Enviro Control, Inc.

Member: Analytical Chemistry Division Energy Conservation Committee

KLATT, L. N.

Member: Program Advisory Committee, Division of Analytical Chemistry, ACS

Associate Editor: *Chemical Instrumentation*

Chairman: Analytical Group of East Tennessee Section, ACS

LAING, W. R.

Chairman: Subcommittee C-26:05, Test Methods, Nuclear Fuel Cycle, ASTM

Coordinator: Analytical Chemistry Division B.S./M.S. Recruiting

Division Representative: ORNL Coal Technology Program Steering Committee UCCND Environmental Control Committee

LYON, W. S.

Member: Committee D-5, Coal and Coke, Subcommittee on Methodology, Task Group on Trace Elements, ASTM

Committee E-10, Nuclear Applications and Measurement of Radiation Effects, ASTM

Subcommittee E-10:01, Fuel Burnup

Subcommittee E-10:05, Dosimetry

Organizing Committee, 6th International Conference on Modern Trends in Activation Analysis

Executive Committee, Isotopes and Radiation Division, ANS

Scientific Committee 25 on Radiation Protection in the Use of Small Neutron Generators, NCRP

Regional Editor: *Journal of Radioanalytical Chemistry*

Associate Editor: *Radiochemical and Radioanalytical Letters*

Program Chairman: Isotopes and Radiation Division, ANS

MASKARINEC, M. P.

Invited Lecturer: Hueston Woods Chromatography Meeting, Cincinnati, Ohio, June 1979

REYNOLDS, S. A.

Member: Committee D-19, Water, ASTM

Committee E-10, Nuclear Technology and Applications, ASTM

Standards Subcommittee ANS-16, Isotopes and Radiation Division, ANS

Technical Advisory Group, ISO Technical Committee 147 on Water Quality

Secretary: D-19 Subcommittee 4, Methods of Radiochemical Analysis, ASTM

Chairman: Working Group 1, Subcommittee 3, ISO Technical Committee 147 on Water Quality

RICCI, E.

Vice Chairmen/Chairman Elect: Isotope and Radiation Division, ANS

Member: National Planning Committee, ANS

ROSS, H. H.

Member: ORNL Graduate Student Selection Panel

ORNL Technology Utilization Committee

Editorial Advisory Board, *Journal of Radioanalytical Chemistry*

Board of Directors, ORNL Credit Union

Chairman: Education Committee, ORNL Credit Union

SHULTS, W. D.

Chairman-elect: Division of Analytical Chemistry, ACS

Analytical Specialist Group, UCC

Member: Technical Services Committee, UCC/ND

ORNL In-Hours Continuing Education Committee

Fellowship Committee, Division of Analytical Chemistry, ACS

	Committee on Environmental Analytical Methodology, ACS
	Editorial Board, *Analytica Chimica Acta*
	Advisory Committee, "Analytical Approach," *Analytical Chemistry*
SMITH, D. H.	
Invited Speaker:	NBS Office of Measurements for Nuclear Safeguards Seminar
WIKE, J. S.	
Secretary-Treasurer:	Analytical Group, East Tennessee Section, ACS

8. PRESENTATION OF RESEARCH RESULTS

As in past years, the division has actively responded to the changing priorities of the ORNL research effort by altering the emphasis of some of its own programs or instituting new studies. The increasing concern with energy – nuclear as well as nonnuclear – is reflected in the research results listed below. The multidisciplinary approach required in many such problems is indicated by the number of papers and talks coauthored by members of other ORNL divisions. Such persons are designated by an asterisk.

PUBLICATIONS

Contributions to Books, Proceedings, and Reports

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Ball, F. L.	Ball, F. L.; Taylor, F. G.;* Parr, P. D.* "Interception and Retention of Simulated Cooling Tower Drift by Vegetation"	*Proc. Symposium on Environmental Effects of Cooling Tower Emissions*, Maryland Dept. of Natural Resources and Water Resources Research Center, Univ. of Maryland, PPSP-CPCTP-22 WRRC Special Report No. 9
Bertram, L. K.	Carter, J. A.; Smith, D. H.; Walker, R. L.; Bertram, L. K. "Analysis of U and Pu Resin Bead Samples with a Single Stage Mass Spectrometer"	*27th Annu. Conf. on Mass Spectrometry and Allied Topics*, Seattle, Wash., June 3-8, 1979, pp. 315-16
Carter, J. A.	Lyon, W. S.; Lindberg, S. E.;* Emery, J. F.; Carter, J. A.; Ferguson, N. M.; Van Hook, R. I.;* Raridon, R. J.;* "Analytical Determination and Statistical Relationship of Forty-One Elements in Coal from Three Coal-Fired Steam Plants"	*Proc. of International Symposium on Nuclear Activation Techniques in the Life Sciences, Vienna, Austria, May 22-26, 1978*, 1979, p. 615
	Carter, J. A.; Donohue, D. L.; Walker, R. L.; Franklin, J. C. "Isotope Dilution Mass Spectrometry of Coal and Fly Ash"	*27th Annu. Conf. on Mass Spectrometry and Allied Topics*, Seattle, Wash., June 3-8, 1979, pp. 403-09

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
	Carter, J. A.; Smith, D. H.; Walker, R. L.; Bertram, L. K. "Analysis of U and Pu Resin Bead Samples with a Single Stage Mass Spectrometer"	*27th Annu. Conf. on Mass Spectrometry and Allied Topics*, Seattle, Wash., June 3-8, 1979, pp. 315-16
Caton, J. E.	Guerin, M. R.; Caton, J. E.; Dalbey, W. E.* "Animal Containment Vessels for Nose-Only Inhalation Bioassay Exposure to Tobacco Smoke"	ORNL-5424, *Tobacco Smoke Inhalation Bioassay Chemistry* (June 1979) pp. 35-46
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Landau, L.	Christie, W. H.; Carter, J. A.; Eby, R. E.; Landau, L.; Musick, W. R. *SSMS Analysis for Boron Contamination on Zircaloy-2 Surfaces Using Ion Implantation Standards as a Calibration Technique*	ORNL/TM-6790 (1979)
Lee, D. A.	Burrell, M. C.;* Lee, D. A. *Analysis of UO_3 Gel Microsphere Decomposition Products by Mass Spectrometry*	ORNL/TM-6649 (January 1978)
	Lee, D. A. *Acid in Perchloroethylene Scrubber Solutions Used in HTGR Chemistry Studies*	ORNL/TM-6750 (January 1979)
	Lee, D. A.; Stinton, D. P.* *Evaluation of Uranium Pyrolysis by Mass Spectrometry*	ORNL/TM-6538 (January 1979)
MacDougall, C. S.	MacDougall, C. S. *Potentiometric Technique for the Determination of Thorium*	ORNL/TM-6604 (January 1979)
	MacDougall, C. S. *Potentiometric Technique for the Determination of Plutonium*	ORNL/CFRP-79/13 (April 1979)
Mamantov, G.	Mamantov, G.; Hinton, E. R.;* Manning, D. L. *Fourier Transform Infrared Spectra of Organophosphorus Compounds*	ORNL/CFRP-79/8 (February 1979)

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Manning, D. L.	Mamantov, G.; Hinton, E. R.;* Manning, D. L. *Fourier Transform Infrared Spectra of Organophosphorus Compounds*	ORNL/CFRP-79/8 (February 1979)
	Manning, D. L. *Reverse-Phase HPLC of Mono- and Di-alkylphosphoric Acids as Phenacyl Naphthacyl Derivatives to Enhance Ultraviolet Detection*	ORNL/TM-6753 (February 1979)
	Manning, D. L. *Reverse-Phase High-Performance Liquid Chromatograph Studies of Trialkylphosphorus Compounds Using Differential Refractive Index*	ORNL/TM-6972 (July 1979)
Marley, J. L.	Marley, J. L.; North, E. D.* *References Sample Plan for Analytical Chemistry and Process Control of the Hot Experimental Facility, Purex Flow Sheet*	ORNL/CFRP-79/30 (August 1979)
Musick, W. R.	Christie, W. H.; Carter, J. A.; Eby, R. E.; Landau, L.; Musick, W. R. *SSMS Analysis for Boron Contamination on Zircaloy-2 Surfaces Using Ion Implantation Standards as a Calibration Technique*	ORNL/TM-6790 (1979)
	Walker, R. L.; Bertram, L. K.; Musick, W. R.; Smith, D. H. *Mass Spectrometry of Plutonium, Uranium, and Thorium*	ORNL/TM-6808 (1979)
Quincy, R. B.	Jenkins, R. A.; Quincy, R. B.; Guerin, M. R. *Selected Constituents in the Smokes of Foreign Commercial Cigarettes: "Tar," Nicotine, Carbon Monoxide, and Carbon Dioxide*	ORNL/TM-6869 (April 1979)
	Jenkins, R. A.; Quincy, R. B.; Guerin, M. R. *Selected Constituents in the Smokes of U.S. Commercial Cigarettes: "Tar," Nicotine, Carbon Monoxide, and Carbon Dioxide*	ORNL/TM-6870 (April 1979)
Reynolds, S. A.	Reynolds, S. A. *Quality Assurance Guide for Nuclear and Radiochemical Analysis*	ORNL/CF-79/173 (May 1979)
Scott, T. G.	Steuber, A. M.;* Edgar, D. E.;* McFadden, A. F.;* Scott, T. G. *Preliminary Investigation of* ^{90}*Sr in White Oak Creek Between Monitoring Stations 2 and 3, Oak Ridge National Laboratory*	ORNL/TM-6510 (December 1978)
Smith, D. H.	Smith, D. H. *New Fortran Computer Programs to Acquire and Process Isotopic Mass Spectrometric Data*	ORNL/TM-7002 (1979)
	Walker, R. L.; Bertram, L. K.; Musick, W. R.; Smith, D. H. *Mass Spectrometry of Plutonium, Uranium, and Thorium*	ORNL/TM-6808 (1979)

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Stewart, J. H.	Stewart, J. H. *Evaluation and Choice of X-Ray Fluorescence Analyzers in Support of Nuclear Fuel Recovery Program*	ORNL/CFRP-79/17 (June 1979)
Stokely, J. R.	Stokely, J. R. *Analytical Chemistry Division Summary Report: Nuclear and Radiochemical Analysis Section*	ORNL/CF-78/396 (December 1978)
	Stokely, J. R. *Analytical Chemistry Division Summary Report: Nuclear and Radiochemical Analysis Section*	ORNL/CF-79/169 (April 1979)
	Guerin, M. R.; Stokely, J. R.; Higgins, C. E.; Griffith, G. W.* *Tobacco Smoke Inhalation Bioassay Chemistry*	ORNL-5424 (June 1979)
	Stokely, J. R. *Analytical Chemistry Division Summary Report: Nuclear and Radiochemical Analysis Section*	ORNL/CF-79/291 (August 1979)
Strain, J. E.	Strain, J. E. *An In-Line Free Acid Monitor for Nuclear Fuel Reprocessing*	ORNL/TM-6800 (May 1979)
Walker, R. L.	Carter, J. A.; Walker, R. L. *Report of Foreign Travel*	ORNL/FTR-718 (October 1979)
	Walker, R. L.; Bertram, L. K.; Musick, W. R.; Smith, D. H. *Mass Spectrometry of Plutonium, Uranium, and Thorium*	ORNL/TM-6808 (1979)
Weinberger, A. J.	Ball, F. L.; Gude, W. D.;* Weinberger, A. J. *Optical and Electron Microscopy Studies of the Retention of Asbestos Fibers in Rat Lung*	ORNL/TM-6827 (April 1979)
Yeatts, L. B.	Griest, W. H.; Yeatts, L. B. *Identification and Quantification of Polynuclear Organic Matter on Particulates from a Coal-Fired Power Plant*	EPRI-EA-1092, Project 1057-1, DOE RTS 77-58, Interim Report, June 1979

ORAL PRESENTATIONS

As in previous years, staff members have made presentations at local, national, and, in a few instances, international meetings. The papers covered a wide variety of subjects, reflecting the division's broad spectrum of activities.

Presentations at Meetings of Professional Societies, Conferences, and the Like

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Bate, L. C.	Bate, L. C. "Determination of Technetium-99 in Mixed Fission Products by Neutron Activation Analysis"	23rd Oak Ridge National Laboratory Conf. on Anal. Chem. in Energy Technology, Gatlinburg, Tenn., Oct. 9-11, 1979
Bostick, D. T.	Bostick, D. T. "Acid Compensated Multiwavelength Determination of Uranium in Process Streams"	Measurement Technology for Safeguards and Material Control Conf., Charleston, S.C., Nov. 26-29, 1979
Caton, J. E.	Caton, J. E.; Maskarinec, M. P.; Henderson, G. M.; Harvey, R. W.; Guerin, M. R.; Barnes, Z. K.* "The Determination of Tracer Compounds by Liquid Scintillation Counting After Preparation of the Samples by Oxidation of the Host Matrix"	1979 Pittsburgh Conf. on Anal. Spectroscopy, Cleveland Convention Ctr., Cleveland, Ohio, Mar. 5-9, 1979
	Caton, J. E.; Griest, W. H.; Yeatts, L. B.; Henderson, G. M.; Tomkins, B. A. The Determination of Polycyclic Aromatic Hydrocarbons on Particulate Matter"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Caton, J. E.; Maskarinec, M. P.; Henderson, G. M. "Separation and Determination of of Harmane and Norharmane by Liquid Chromatographic Techniques"	33rd Tobacco Chemists' Res. Conf., Lexington, Ky., Oct. 29-31, 1979
Carter, J. A.	Carter, J. A. "Major and Minor Uranium and Plutonium Isotopic Measurements for Isotopic Correlation Studies"	Brookhaven National Laboratory, Upton, N.Y., June 19, 1979
Christie, W. H.	White, C. W.;* Christie, W. H.; Pronko, P. P.;* Appleton, B. R.;* Wilson, S. R.;* Wang, J. C.;* Wood, R. F.;* Magee, C. W.* "Changes in Dopant Profiles by Pulsed Laser Annealing of Ion Implanted Silicon"	Catania, Italy, Aug. 31-Sept. 2, 1978
	Young, R. T.;* Wood, R. F.;* Narayan, J.;* Christie, W. H. "Laser Techniques in Photovoltaic Application"	23rd Annu. Tech. Symp., Soc. of Photo-Optical Instrum. Eng., San Diego, Calif., Aug. 27-30, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Christie, W. H.	Wood, R. F.;* Young, R. T.;* Westbrook, R. D.;* Narayan, J.;* Christie, W. H. "New Techniques for the Study and Control of Grain Boundary Effects"	Photovoltaic Material and Device Measurement Workshop, Arlington, Va., June 11-13, 1979
	Young, R. T.;* White, C. W.;* Narayan, J.;* Christie, W. H. "Characterization of Laser-Annealed, Ion-Implanted Polycrystalline Si"	Poster Session, Photovoltaic Material and Device Measurement Workshop, Arlington, Va., June 11-13, 1979
	Landau, L.; Carter, J. A.; Christie, W. H. "Mass Spectroscopic Methodology for Characterizing Doped Nobel Metal Alloys"	Nat. Am. Chem. Soc. Mtg., Washington, D.C., Sept. 10-14, 1979
	Christie, W. H.; Eby, R. E.; Kollie, T. G.* "A Quantitative SIMS Analysis of Decalibrated Chromel Versus Alumel Thermocouples Using Indexed Sensitivity Factors"	27th Annu. Conf. on Mass Spectrometry and Allied Topics, Seattle, Wash., June 3-8, 1979
	Christie, W. H.; White, C. W.* "SIMS Depth Profiling Studies: The Effect of Laser Annealing on the Distribution of Ion Implanted Boron in Silicon"	Invited Talk, 7th Canadian Seminar on Surfaces, Pinawa, Manitoba, Canada, June 11-13, 1979
	Christie, W. H.; Warmack, R. J.; White, C. W.* "Laser Induced Redistribution of Ion Implanted and Surface Deposited B in Silicon: A SIMS Study"	2nd International Conf. on Secondary Ion Mass Spectrometry, Palo Alto, Calif., Aug. 26-31, 1979
	Christie, W. H.; Eby, R. E.; Warmack, R. J. "Secondary Ion Mass Spectrometry"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Christie, W. H. "Ion Implantation Standards for Research and Surface Analysis"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
Clark, B. R.	Clark, B. R.; Ho, C.-h.; Guerin M. R. "Isolation and Identification of Mutagenic Amines in Complex Mixtures"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
Costanzo, D. A.	Costanzo, D. A. "Analytical CHemistry Development in Support of the Consolidated Fuel Reprocessing Program"	USDOE/USAERE Fast Breeder Information Exchange Meeting, Dounreay, Scotland, May 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Costanzo, D. A.	Costanzo, D. A. "Analytical Chemistry Development for the Advanced Fuel Recycle Program"	CFRP Information Exchange Meeting, Savannah River Laboratory, Aiken, S.C., Jan. 1979
	Costanzo, D. A. "CFRP Analytical Development—An Overview"	CFRP Technical Review Meeting, Oak Ridge National Laboratory, Oak Ridge, Tenn., Oct. 1979
	Costanzo, D. A. "Analytical Chemistry in Support of the United Kingsom Fast Breeder Reactor Program"	CFRP Seminar, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1979
Dalbey, W. E.*	Dalbey, W. E.*; Nettesheim, P.; Griesemer, R.;* Caton, J. E.; Guerin, M. R. "Chronic Inhalation of Cigarette Tobacco Smoke by Rats"	19th Annu. Hanford Life Sci. Symp.: Pulmonary Toxicology of Respirable Particles, Richland, Wash., Oct. 22-24, 1979
Dale, J. M.	Dale, J. M.; Hulett, L. D.; Pendyala, S.* "A Study of a High-Yield Positron Moderator Surface"	Conf. on Chem. and Phys. Properties of Solid Surfaces, Lake Geneva, Wis., Oct. 29-31, 1979
Donohue, D. L.	Donohue, D. L.; Carter, J. A.; Walker, R. L. "Isotope Dilution Mass Spectrometry of Coal and Fly Ash"	27th Conf. on Mass Spectrometry and Allied Topics, Seattle, Wash., June 3-8, 1979
	Donohue, D. L. "Channel Electron Multiplier Array Detector for SSMS"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
Dyer, F. F.	Dyer, F. F. "The Use of Neutron Activation Analysis in Criminalistics - a Look at the Past and a Peek at the Future"	ORAU Traveling Lecture Ser., Sam Houston State Univ., Huntsville, Tex., Feb. 1979
	Dyer, F. F. "The Use of Neutron Activation Analysis in Criminalistics - a Look at the Past and a Peek at the Future"	ORAU Traveling Lecture Ser., Univ. of Arkansas, Pine Bluff, Ark., Feb. 1979
	Dyer, F. F. "ANGEL: A Conversational Program for Nuclear Fuel Element Scanning by Ge(Li) Gamma Spectroscopy"	Conf. on Computers in Activation Analysis and Gamma-Ray Spectroscopy, Mayaguez, Puerto Rico, May 1-4, 1978

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Dyer, F. F.	Dyer, F. F.; Wichner, R. P.* "A Study of the Behavior of Tritium in the Peach Bottom HTGR"	Am. Nucl. Soc. Winter Mtg., San Francisco, Calif., Nov. 11-16, 1979
Eatherly, W. P.*	Rubin, I. B.; Griest, W. H.; Eatherly, W. P.* "Preparation and Relative Aromatic Composition of Petroleum and Coal Tar Pitch Extracts for Mutagenicity Testing"	14th Biennial Conf. on Carbon, Pennsylvania State Univ., State College, Pa., June 25-29, 1979
Eldridge, J. S.	Eldridge, J. S.; Oakes, T. W.;* Shank, K. E.* "Instrumental Methods Used in Environmental Surveillance Programs Around a Low-Level Radioactive Burial Site"	Health Phys. Soc. 12th Midyear Topical Symp., Low-Level Radioactive Waste Management, Williamsburg, Va., Feb. 12-15, 1979
	Eldridge, J. S.; Oakes, T. W.;* Shank, K. E.* "Specific Radionuclide Analyses Applied to Air-Monitoring Samples"	Am. Nucl. Soc., 25th Annu. Mtg., Atlanta, Ga., June 3-8, 1979
	Eldridge, J. S. "Report on Three Mile Island"	Anal. Chem. Div. Seminar, Oak Ridge National Laboratory, Oak Ridge, Tenn., April 1979
	Eldridge, J. S.; Bronfman, L.;* Chester, C. V.;* Weinberg, A. M.* "Three Mile Island and Civil Defense"	Oak Ridge Civil Defense Soc. Mtg., Oak Ridge, Tenn., May 30, 1979
	Oakes, T. W.;* Eldridge, J. S.; Shank, K. E.* "Investigation of ^{137}Cs, ^{60}Co and ^{90}Sr Concentrations in Water and Sediment as a Function of Flow in White Oak Creek"	Health Phys. Soc. Annu. Mtg., Philadelphia, Pa., July 8-13, 1979
	Oakes, T. W.;* Shank, K. E.;* Eldridge, J. S. "Highlights of Applied Analytical Methodology to Environmental Surveillance at the Oak Ridge National Laboratory"	22nd Conf. on Anal. Chem. in Energy Technology, Gatlinburg, Tenn., Oct. 9-12, 1978
	Oakes, T. W.;* Shank, K. E.;* Eldridge, J. S. "Quality Assurance as Applied to Environmental Surveillance"	Western Occup. Health Conf., Los Angeles, Calif., Oct. 15-19, 1978
	Shank, K. E.;* Oakes, T. W.;* Eldridge, J. S. "Evaluation of Radiation Impacts on Man in East Tennessee"	106th Annu. Mtg. of the Am. Public Health Assoc. Los Angeles, Calif., Oct. 15-19, 1978
Griest, W. H.	Griest, W. H.; Maskarinec, M. P.; Herbes, S. E.;* Southworth, G. R.* "Multicomponent Methods for the Identification and Quantification of Polycyclic Aromatic Hydrocarbons in the Aqueous Environment"	ASTM D-19.33 Mtg. on the Anal. of Waters Associated with Alternate Fuel Production, Pittsburgh, Pa., June 4-8, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Griest, W. H.	Griest, W. H.; Caton, J. E.; Guerin, M. R.; Yeatts, L. B.; Higgins, C. E. "Extraction and Recovery of Polycyclic Aromatic Hydrocarbons for Quantitation"	4th International Symp. on Polycyclic Aromatic Hydrocarbons, Columbus, Ohio, Oct. 2-4, 1979
	Griest, W. H.; Maskarinec, M. P.; Burnett, E. M. "Chemical Characterization of Solid Wastes for Environmental Assessment"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Griest, W. H.; Guerin, M. R. "The USEPA/DOE Fossil Fuels Research Materials Facility: Distribution of Paraho Oil Shale and SOHIO-Refined Paraho Oil Materials"	EPA/ORNL Repository Mtg.: A Matrix Approach to Biological Investigation of Synfuels, Research Triangle Park, N.C., April 26, 1979
Guerin, M. R.	Guerin, M. R. "Mutagenic Constituents of Synthetic Oils"	BETC 1979 Seminar on Fossil Energy Research, Bartlesville Energy Technology Center, Bartlesville, Okla., May 22, 1979
	Guerin, M. R.; Clark, B. R.; Ho, C.-h. "Quest for Determinant Mutagens in Synfuels"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Guerin, M. R.; Clark, B. R.; Griest, W. H. "Chemical Characterization in Petroleum Identification"	Nat. Am. Chem. Soc. Mtg., Washington, D.C., Sept. 9-14, 1979
	Guerin, M. R. "Mutagenic Constituents of Synthetic Oils"	Invited Seminar at E. I. du Pont de Nemours Co., Wilmington, Del., May 30, 1979
	Guerin, M. R. "Chemical Composition of Cigarette Smoke"	Invited Speaker, Banbury Mtg. - Toward a Less Hazardous Cigarette, Cold Spring Harbor, N.Y., Oct. 14-16, 1979
Haire, R. G.*	Young, J. P.; Bourges, J. Y.;* Haire, R. G.;* Peterson, J. R.* "On the Triiodides of Americium"	Nat. Am. Chem. Soc. Mtg., Washington, D.C., Sept. 9-14, 1979
	Young, J. P.; Haire, R. G.;* Bourges, J. Y.* "Absorption Spectrometric and X-Ray Diffraction Studies of NdI_3, NdOI and SmI_3"	14th Rare Earth Res. Conf., Fargo, N. Dak., June 25-28, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Haschek, W. M.*	Haschek, W. M.;* Boling, M. E.;* Guerin, M. R.; Witschi, H. P.* "Pulmonary Toxicity of a Coal Liquefaction Distillate Product"	19th Annu. Hanford Life Sci. Symp.: Pulmonary Toxicology of Respirable Particles, Richland, Wash., Oct. 22-24, 1979
Herbes, S. E.*	Herbes, S. E.;* Southworth, G. R.;* Shaeffer, D. L.;* Griest, W. H.; Maskarinec, M. P. "Critical Pathways of Polycyclic Aromatic Hydrocarbons in Aquatic Environments"	Symp. on Sci. Base of Toxicity Assessment, Gatlinburg, Tenn., April 15-19, 1979
Hieftje, G. M.*	Hieftje, G. M.;* Ramsey, J. M.; Havgen, G. R.* "A New, Simple Method for Measuring Atomic and Molecular Excited-State Lifetimes"	8th International Conf. on Atomic Spectroscopy, Cambridge, England, July 3, 1979
Higgins, C. E.	Higgins, C. E.; Guerin, M. R. "Recovery of Diaromatics During Evaporative Concentration"	Southeastern Regional Mtg., Am. Chem. Soc., Roanoke, Va., Oct. 24-26, 1979
Ho, C.-h.	Ho, C.-h.; Clark, B. R.; Guerin, M. R.; Ma, C. Y.;* Rao, T. K.* "Aromatic Nigrogen Compounds in Fossil Fuels--A Potential Hazard?"	Nat. Am. Chem. Soc. Mtg., Honolulu, Hawaii, Apr. 1-7, 1979
Holland, J. M.	Holland, J. M.;* Rahn, R. O.;* Smith, L. H.;* Clark, B. R.; Chang, S. S.;* Stephens, T. J.* "Dosimetry of Coal and Shale Derived Crude Liquids as Mouse Skin Carcinogens"	EPA Oil Shale Sampling, Analysis, and Quality Assurance Symp., Denver, Colo., March 26-28, 1979
Hulett, L. D.	Hulett, L. D. "The Use of Electron Spectroscopy and Scanning Electron Microscopy for Surface Analysis"	ORAU Taveling Lecture, Auburn Univ., Auburn, Ala., Jan. 19, 1979
	Hulett, L. D.; Weinberger, A. J. "On the Chemical Speciation of Fly Ash: Some Studies of Matrix Composition and Structure and the Distribution of Trace Elements"	21st Rocky Mountain Conf. on Anal. Chem., Denver, Colo., July 30-Aug. 1, 1979
	Hulett, L. D.; Weinberger, A. J.; Emery, J. F. "Chemical Speciation of Fly Ash"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Hulett, L. D.; Dale, J. M. "A Discussion of Some XPS Fundamentals that Commonly Apply to Problem Solving"	Conf. on Chem. and Phys. Prop. of Solid Surfaces, Lake Geneva, Wis., Oct. 29-31, 1979
	Hulett, L. D. "Principles of XPS and SEM-EDX"	Invited Speaker, Univ. Nac. Auton. de Mex., Inst. de Fis., Nov. 13, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Hulett, L. D.	Hulett, L. D. "Design of Monoenergetic Positron Sources and Their Research Applications"	Invited Speaker, Univ. Nac. Auton. de Mex., Inst. de Fis., Nov. 14, 1979
	Hulett, L. D. "Theory and Operation of the Scanning Electron Microscope"	Invited Speaker, Oak Ridge Assoc. Univ., Dec. 14, 1979
	Hulett, L. D. "Applications of the Scanning Electron Microscope"	Invited Speaker, Oak Ridge Assoc. Univ., Dec. 14, 1979
	Hulett, L. D. "Scanning Microscope Operation and Interpretation"	Invited Speaker, Oak Ridge Assoc. Univ., Dec. 15, 1979
Hurst, G. S.*	Young, J. P.; Hurst, G. S.;* Kramer, S. D.;* Payne, M. C.* "Detection of the Daughter Atoms in Radioactive Decay"	Invited paper, Symp. on Radionuc. in Earth and Space Sci., honoring Ray Davis - Am. Chem. Soc., Washington, D.C., Sept. 9-14, 1979
	Young, J. P.; Hurst, G. S.;* Kramer, S. D.;* Payne, M. G.* "A Generalization of One-Atom Detection"	Am. Phys. Soc., Washington, D.C., April 23-26, 1979
Jenkins, R. A.	Jenkins, R. A.; Quincy, R. B.; Guerin, M. R.; Maskarinec, M. P. "Analytical Chemistry Development and Support for the NCI S&HP"	1979 Nat. Cancer Inst. Smoking and Health Program Contractors' Mtg., Savannah, Ga., Mar. 12-14, 1979
	Jenkins, R. A.; Gayle, T. M.;* "An Instrumental Inhaled Smoke Dosimeter for the Quantitative Characterization of Aerosol Exposures"	19th Annu. Hanford Life Sci. Symp: Pulmonary Toxicology of Respirable Particles, Richland, Wash., Oct. 22-24, 1979
	Jenkins, R. A.; Caton, J. E.; Maskarinec, M. P.; Gayle, T. M.;* Guerin, M. R. "Analytical and Instrumental Support of the NCI Tobacco Smoke Inhalation Bioassays"	1979 Nat. Cancer Inst. Smoking and Health Program Contractors' Mtg., Savannah, Ga., Mar. 12-14, 1979
	Jenkins, R. A.; Quincy, R. B.; Guerin, M. R. "Carbon Monoxide Deliveries of Commercial Cigarettes: Relationship to Other Smoke Constituents"	33rd Tobacco Chemists' Res. Conf., Lexington, Ky., Oct. 29-31, 1979

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Klatt, L. N.	Klatt, L. N. "Remote Analytical Instrumentation"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
Laing, W. R.	Laing, W. R.; Corbin, L. T. "Radioactive Materials Analytical Laboratory"	Am. Nucl. Soc. Mtg., San Francisco, Calif., Nov. 11-15, 1979
Landau, L.	Landau, L.; Carter, J. A.; Christie, W. H.; Eby, R. E.; Franklin, J. C.* "Mass Spectroscopic Methodology for Characterizing Doped Noble Metal Alloys"	Nat. Am. Chem. Soc. Mtg., Washington, D.C., Sept. 9-14, 1979
Lee, D. A.	Lee, D. A. "Evaluation of Urania Gel Pyrolysis by Mass Spectrometry"	Nat. Am. Chem. Soc. Mtg., Washington, D.C., Sept. 9-14, 1979
Lyon, W. S.	Lyon, W. S. "A Scientometric Study of IAEA Activation Analysis Conferences"	Am. Nucl. Soc. Mtg., San Francisco, Calif., Nov. 11-15, 1979
Mamantov, G.	Mamantov, G.; Marassi, R.;* Matsunaga, M.;* Tanemoto, K.;* Ogata, Y.;* Frazer, E. J.;* Wiaux, J. P.;* Norvell, V. E.; Klatt, L. N. "Electrooxidation of Sulfur in Molten Chloroaluminates: Applications to a Rechargeable Molten Salt Battery"	Nat. Am. Chem. Soc. Mtg., Washington, D.C., Sept. 9-14, 1979
Manning, D. L.	Manning, D. L. "Liquid Chromatographic and Gas Chromatographic Studies of Organophosphorous Compounds"	Nat. Am. Chem. Soc. Mtg., Honolulu, Hawaii, Apr. 1-7, 1979
	Manning, D. L.; Maskarinec, M. P.; Harvey, R. W. "High Performance Liquid Chromatographic Studies of Low Molecular Weight Carbonyl Compounds in Tobacco Smoke"	33rd Tobacco Chemists' Res. Conf., Lexington, Ky., Oct. 29-31, 1979
Maskarinec, M. P.	Maskarinec, M. P. "Practical Aspects of Glass Capillry Gas Chromatography"	UCC Gas Chromatogr. Specialists' Group Mtg., Pittsburgh, Pa., Mar. 6, 1979
	Maskarinec, M. P.; Olerich, G.; Harvey, R. W.; Harmon, S. H.; "Factors Affecting the Thermal Stability of Glass Capillary Columns"	Hueston Woods Chromatogr. Mtg., Cincinnati, Ohio, June 20-22, 1979
	Maskarinec, M. P.; Olerich, G.; Gonnord, M. F.;* Harvey, R. W. "Advances in Glass Capillary Gas Chromatography"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979

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Maskarinec, M. P.	Maskarinec, M. P.; Guerin, M. R. "Preparation of Glass Capillary Columns for the Gas Chromatographic Analysis of Tobacco Smoke Constituents"	33rd Tobacco Chemists' Res. Conf., Lexington, Ky., Oct. 29-31, 1979
	Maskarinec, M. P. "Preparation of High-Efficiency Glass Capillary Columns for Gas Chromatography"	UCC Anal. Specialists' Group Mtg., Charleston, W. Va., Oct. 26, 1979
	Maskarinec, M. P. "Chromatographic Techniques in Environmental Analysis"	UCC Anal. Specialists' Group Mtg., Charleston, W. Va., Oct. 26, 1979
MacDougall, C. S.	MacDougall, C. S. "Use of HP-9825-A for Computer Control of Instrumentation and Acquistion and Analysis of Data"	In-house Seminar, Oak Ridge National Laboratory, Jan. 1979
	MacDougall, C. S.; Roberson, R. B.* "Kinetics of the Nitric Acid-Sugar Reaction: Acid Kill"	In-house Seminar, Oak Ridge National Laboratory, Aug. 1979
Narayan, J.*	Narayan, J.;* Larson, B. C.;* Christie, W. H. "Effect of Thermal Annealing in Boron Implanted, Laser Annealed Silicon"	Laser-Solid Interations Laser Processing Symp. Boston, Mass., Nov. 28-Dec. 1, 1978
Rainey, W. T.	Rainey, W. T.; Pritchard, C. A.; Higgins, C. E.; Moneyhun, J. H.; "Sampling and Analysis of Trace Organics in Air"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
Ramey, D. W.*	Ramey, D. W.;* Epler, J. L.;* Rao, T. K.;* Maskarinec, M. P. "Application of Mutagenicity Testing to Urine Samples of Animals Exposed to Cigarette Smoking"	10th Annu. Mtg., Environ. Mutagen Soc., New Orleans, La., Mar. 8-12, 1979
Ramsey, J. M.	Ramsey, J. M. "New Approaches to Luminescence Lifetime Determinations"	Invtied Talk, Univ. of Tennessee, Knoxville, Tenn., May 29, 1979
Rao, T. K.*	Rao, T. K.;* Ellis, K. B.;* Tipton, S. C.;* Epler, J. L.;* Griest, W. H. "Multialkylated Polycyclic Aromatic Hydrocarbons in Energy Related Materials: Biological Activity in the Ames Salmonella Assay"	10th Annu. Mtg., Environ. Mutagen Soc., New Orleans, La., Mar. 8-12, 1979
	Rao, T. K.;* Epler, J. L.;* Schmidt-Collerus, J. J.;* Leffler, L.;* Guerin, M. R. "Biological Monitoring of Oil Shale Products and Effluents Using Short-Term Genetic Analyses"	Oil Shale Sampling, Analyses and Quality Assurance Symp., Denver, Colo., Mar. 26-28, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Reynolds, S. A.	Reynolds, S. A.; Eldridge, J. S. "Investigation of Cerenkov Counting of Environmental Strontium-90"	International Conf. on Liquid Scintillation Counting, San Francisco, Calif., Aug. 21-24, 1979
	Reynolds, S. A. "Quality Assurance in Radiochemistry"	Seminar, Earth Sci. Sec., Environ. Sci. Div., Oak Rdige National Laboratory, Oak Ridge, Tenn., June 28, 1979
	Reynolds, S. A. "ORNL Participation in DOE Quality Assessment Programs"	DOE Environ. Management Appraisal of ORNL, Oak Ridge National Laboratory, Oak Ridge, Tenn., Oct. 17, 1979
	Reynolds, S. A. "Cerenkov Counting in Environmental Radioanalysis"	Seminar for Visiting Finnish Scientists, Oak Ridge National Laboratory, Oak Ridge, Tenn., Oct. 25, 1979
Ross, H. H.	Ross, H. H. "Recent Applications of Cerenkov Counting"	International Conf. on Liquid Scintillation Counting, San Francisco, Calif., Aug. 21-24, 1979
Rubin, I. B.	Rubin, I. B.; Goeckner, N. A.; Clark, B. R. "Polar Constituents of a Shale Oil: Comparative Composition with Other Fossil-Derived Liquids"	Oil Shale Sampling, Analysis and Quality Assurance Symp., Denver, Colo., Mar. 26-28, 1979
	Rubin, I. B.; Griest, W. H.; Eatherly, W. P.;* "Preparation and Relative Aromatic Composition of Petroleum and Coal Tar Pitch Extracts for Mutagenicity Testing"	14th Biennial Conf. on Carbon, Pennsylvania State Univ., June 25-29, 1979
Russell, D. H.	Russell, D. H.; Canada, D. C.; McBay, E. H. "Some Aspects of the Unimolecular Decarbonylation Reaction of C_7H_7O"	27th Annu. Conf. on Mass Spectrometry and Allied Topics, Seattle, Wash., June 3-8, 1979
	Russell, D. H.; Canada, D. C.; Rainey, W. T. "Metastable Ion Methods--IKES and MIKES--As Structural Probes for the Study of Gas-Phase Organic Ions"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Russell, D. H.; Smith, D. H.; Warmack, R. J. "A Novel Mass Spectrometer for Ion Kinetic Energy Spectrometry (MIKES)"	Nat. Am. Chem. Soc. Mtg., Washington, D.C., Sept. 9-14, 1979
	Russell, D. H.; Smith, D. H.; Warmack, R. J. "A Novel Mass Spectrometer for the Study of Field-Free Region Ion Chemistry"	27th Annu. Conf. on Mass Spectrometry and Allied Topics, Seattle, Wash., June 3-8, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Russell, D. H.	Russell, D. H.; Gross, M. L.* "Electrocycle Ring Opening of the Cyclobutene Radical Cation"	27th Annu. Conf. on Mass Spectrometry and Allied Topics, Seattle, Wash., June 3-8, 1979
	Russell, D. H. "MS/MS at ORNL"	UCC Anal. Specialists' Mtg., Charleston, W. Va., Oct. 26, 1979
	Russell, D. H.; Gross, M. L.* "Decomposition of the 1,3-Butadiene Cation on the Microsecond to Picosecond Time Scale"	27th Annu. Conf. on Mass Spectrometry and Allied Topics, Seattle, Wash., June 3-8, 1979
Scott, T. G.	Scott, T. G. "Low-Level Radiochemistry"	Anal. Committee Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 7, 1979
Shaw, R. W.	Shaw R. W. "Pulsed Dye Laser OAS with a Helmholtz Resonator Cell"	Topical Mtg. on Photoacoustic Spectroscopy, Iowa State Univ., Ames, Iowa, Aug. 1-3, 1979
	Shaw, R. W. "Helmholtz Resonator Cells for Pulsed Optoacoustic Spectroscopy and Radiometry"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
Sherman, R. L.	Sherman, R. L.; Vallet, C. E.;* Heatherly, D. E.;* Braunstein, J.* "Concentration Profiles from Electrolysis in a Model System for Molten Salt Batteries"	Electrochem. Soc. Fall Mtg., Los Angeles, Calif., Oct. 14-19, 1979
Smith, D. H.	Smith, D. H.; Walker, R. L.; Bertram, L. K.; Carter, J. A. "Analyses of Resin Bead Samples with a Single Stage Mass Spectrometer"	27th Annu. Conf. on Mass Spectrometry and Allied Topics, Seattle, Wash., June 3-8, 1979
	Smith, D. H.; Walker, R. L.; Carter, J. A. "Resin Beads, Mass Spectrometry, and Safeguards: A New Technique for Isotopic and Quantitative Analysis of Small U and Pu Samples"	Invited Seminar at Nat. Bureau of Standards, Washington, D.C., Mar. 29, 1979
	Smith D. H. "Mass Spectrometric R/D for Safeguards"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Stewart, J. H.	Stewart, J. H. "X-Ray Fluorescence - Inductively Coupled Plasma Spectroscopic Studies of TVA Fly Ash"	Invited Speaker, ASTM D-5 Coal and Coke Committee Mtg., Williamsburg, Va., May 14-15, 1979
Strain, J. E.	Strain, J. E. "An In-Line Free Acid Monitor for Nuclear Fuel Reprocessing"	23rd Conf. on Anal. Chem. in Energy Technology, Gatlinburg, Tenn., Oct. 9-11, 1979
Walker, R. L.	Walker, R. L.; Smith, D. H. "Analysis of Plutonium and Uranium by the Resin Bead Mass Spectrometric Method"	Invited Paper, Am. Nucl. Soc. Conf. on Measurement Techn. for Safeguards and Mat. Control, Charleston, S.C., Nov. 26-29, 1979
	Walker, R. L. "Development of Resin Bead-Isotope Dilution-Mass Spectrometric Techniques for Tc-99 Analysis"	23rd Conf. on Anal. Chem. in Energy Technology, Gatlinburg, Tenn., Oct. 9-11, 1979
Warmack, R. J.	Stockdale, J. A. D.;* Warmack, R. J. "Collisional Ionization of Ca and K by O_2"	7th International Symp. on Molecular Beams, Riva del Garda, Italy, June 1979
Whitten, W. B.	Whitten, W. B.; Ross, H. H. "Time-of-Flight Spectroscopy with Fiber Optic Waveguides"	CLEA Mtg., Washington, D.C., May 30-June 1, 1979
	Whitten, W. B.; Ross, H. H. "Applications of Fiber Optics in Absorption Spectrometry"	6th Annu. Mtg. Federation of Anal. Chem. and Spectroscopy Soc., Philadelphia, Pa., Sept. 16-21, 1979
	Whitten, W. B.; Ross, H. H. "Time-of-Flight Spectroscopy with Fiber Optic Wavelengths"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Whitten, W. B.; Ross, H. H. "Spectroscopic Applications of Fiber Optics"	Gordon Research Conf., N.H., Aug. 1979
Yeatts, L. B.	Yeatts, L. B.; Griest, W. H. "A Comparison of the Chemical and Physical Characteristics of Retorted Oil Shale Particulates and Coal Fly Ash"	Southeastern Regional Mtg., Am. Chem. Soc., Roanoke, Va., Oct. 24-26, 1979

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Young, J. P.	Young, J. P. "Analytical Applications of Resonance Ionzation Spectroscopy"	DBER Contractors' Workshop on Advanced Laser Technology for Pollutant Measurements, Lawrence Berkeley Laboratory, Feb. 7-8, 1979
	Young, J. P.; Hurst, G. S.;* Kramer, S. D.;* Payne, M. G.* "Analytical Applications of Resonance Ionization Spectroscopy"	Gordon Research Conf., N.H., Aug. 1979
	Young, J. P.; Haire, R. G.;* Ensor, D. D.;* Peterson, J. R.* "Effect of Cover Gas and Temperature on the Chemical Consequences of α and β in the Halide Series: Es —>Bk —>Cf"	Nat. Am. Chem. Soc. Mtg., Honolulu, Hawaii, Apr. 1-7, 1979
	Young, J. P.; Kramer, S. D.;* Payne, M. G.;* Hurst, G. S.* "The Determination of Lithium by Resonance Ionization Spectroscopy"	Nat. Am. Chem. Soc. Mtg., Honolulu, Hawaii, Apr. 1-7, 1979
	Young, J. P. "Spectrophotometric Study of the Chemical Consequences of Radioactive Decay"	ACD Information Mtg., Oak Ridge National Laboratory, Oak Ridge, Tenn., June 18-20, 1979
	Young, J. P. "Specific Detection of Atoms, One at a Time"	Huntington College, Huntington, Ind., Oct. 30, 1979
	Young, J. P. "Single Atom Detectors"	Taylor Univ., Upland, Ind., Oct. 29, 1979
	Young, J. P.; Kramer, S. D.;* Hurst, G. S.;* Payne, M. G.;* Callcott, T. A.;* Arakawa, D. T.;* Beekman, D. W.* "Applications of Resonance Ionization Spectroscopy to Ultra-low-Level Counting"	10th International Radiocarbon Conf. in Berne and Heidelberg, Heidelberg, Switzerland, Aug. 19-26, 1979
	Young, J. P. "Specific Detection of Atoms, One at a Time"	Invited talk, Tennessee Technological Univ., Cookeville, Tenn., May 8, 1979

ANALYTICAL CHEMISTRY DIVISION SEMINARS AT ORNL

Speaker	Title	Date
Etz, E. S. National Bureau of Standards, Washington, D.C.	"Molecular Microanalyses with the NBS Raman Microprobe"	Jan. 18, 1979
Cram, S. T. Varian Instrument Div., Walnut Creek, Calif.	"New Techniques for High Resolution Chromatographic Analyses	Feb. 27, 1979
Gross, M. L. Dept. of Chem., Univ. of Nebraska, Lincoln, Neb.	"Some Recent Applications of High Performance Mass Spectrometry: Ultra Trace Organic Analyses, Gas Phase Organic Reaction Mechanisms, and Metastable Ion Methods"	Mar. 20, 1979
Stohr, J. Stanford Synchrotron Radiation Lab., Stanford, Calif.	"EXAFS and Surface EXAFS Studies Above the K Edges of Nitrogen and Oxygen"	Apr. 17, 1979
Horlick, G. Univ. of Alberta, Canada	"Simultaneous Multi-Element Analyses Using Atomic Emission Sources and a Fourier Transform Spectrometer"	May 14, 1979
Swaine, D. J. Geoscience Unit, Australia	"Trace Elements in Australian Coal"	June 12, 1979
Lytle, F. E. Purdue Univ., W. Lafayette, Ind.	"The Use of Lasers in Applied Spectroscopy"	July 10, 1979
Cooks, R. G. Purdue Univ., W. Lafayette, Ind.	"Mass-Analyzed Ion Kinetic Energy Spectrometry (MIKES); Fundamentals and Analytical Applications"	July 17, 1979
Hume, D. N. M.I.T., Cambridge, Mass.	"The Reliability of Environmental Trace Analyses"	Oct. 23, 1979
Sievers, R. Univ. of Colorado, Boulder, Colo.	"Selective Electron Capture Sensitization; Chromatographic Studies of Environmental Pollutants"	Nov. 12, 1979
Trombka, J. I. Lab. for Astronomy and Solar Physics, NASA-Goddard Space Flight Center, Greenbelt, Md.	"Exploring the Universe with Gamma-Rays"	Dec. 6, 1979

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

Reviewer or referee	*Anal. Chem.*	*Anal. Chim. Acta*	*Anal. Biochem.*	ANSI Methods	ASTM Methods	*Environ. Sci. Technol.*	EPA Reports	*J. Environ. Qual.*	*Mol. Cryst. Liq. Cryst.*	ORNL Reports	Proceedings	Proposals	*Radiochem. Radioanal. Lett.*	Total
Christie, W. H.	1										3	2		6
Costanzo, D. A.										2				2
Feldman, C.	8				6									14
Holmberg, R. W.						1								1
Hulett, L. D.	1					2						1		4
Klatt, L. N.	5									2				7
Laing, W. R.										2				2
Lyon, W. S.	6	1	1			2						3	3	16
MacDougall, C. S.	1													1
Manning, D. A.	3													3
Mueller, T. R.	1													1
Ramsey, J. M.	2											1		3
Reynolds, S. A.				2	2		1				2			7
Shaw, R. W.												1		1
Shults, W. D.		1				1						3		5
Smith, D. H.												1		1
Stewart, J. H.								1		1		1		3
Whitten, W. B.									1					1
Young, J. P.	1										1	2		4
Total	29	2	1	2	8	6	1	1	1	7	6	15	3	82

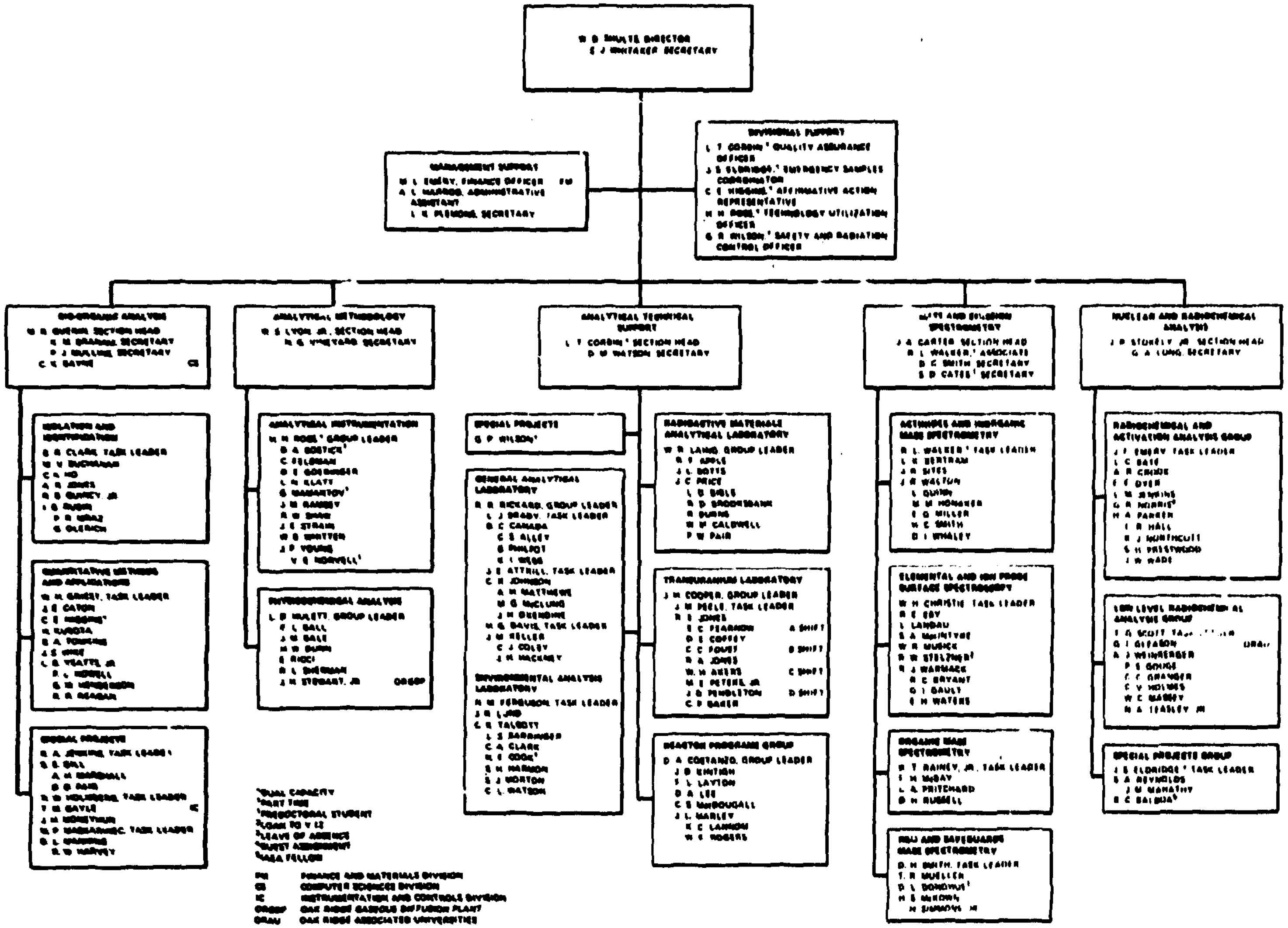
DIVISIONAL MAN-POWER AND FINANCIAL SUMMARY
FY 1979

	Funding (in thousands)	Man-years
DOE programs		
Basic Energy Sciences	994	14.0
Environment Research and Development	1,033	15.5
Nuclear Materials Security and Safeguards	150	2.0
Consolidated Fuel Reprocessing Program	512	7.5
Reactor Research and Development	113	1.5
Total DOE Programs	2,802	40.5
Work for others – federal agencies		
National Cancer Institute	619	9.5
Department of Defense (U.S. Army)	45	1.0
Environmental Protection Agency	663	10.0
State Department (I.S.P.O.)	129	2.5
Miscellaneous	60	1.0
Total work for others–federal agencies	1,516	24.0
Work for others – nonfederal agencies		
Council for Tobacco Research	194	3.5
TRFR (Thermal Reactor Fuel)	50	1.0
Electric Power Research Institute	117	2.0
Protective coating companies	78	1.5
Westinghouse Electric Corporation	21	0.5
Miscellaneous	50	1.0
Total work for others–nonfederal agencies	510	9.5
ORNL Divisions – support	4,971[a]	76.0
Others	570[a]	10.0
Total financial plans	10,369	160.0

[a] Reflects Laboratory General and Administrative–General Plant Services.

ANALYTICAL CHEMISTRY DIVISION

JANUARY 1, [illegible]



[1] DUAL CAPACITY
[2] PART TIME
[3] PREDOCTORAL STUDENT
[4] LOAN TO Y-12
[5] LEAVE OF ABSENCE
[6] GUEST ASSIGNMENT
[7] NASA FELLOW

FM	FINANCE AND MATERIALS DIVISION
CS	COMPUTER SCIENCES DIVISION
IC	INSTRUMENTATION AND CONTROLS DIVISION
ORGDP	OAK RIDGE GASEOUS DIFFUSION PLANT
ORAU	OAK RIDGE ASSOCIATED UNIVERSITIES