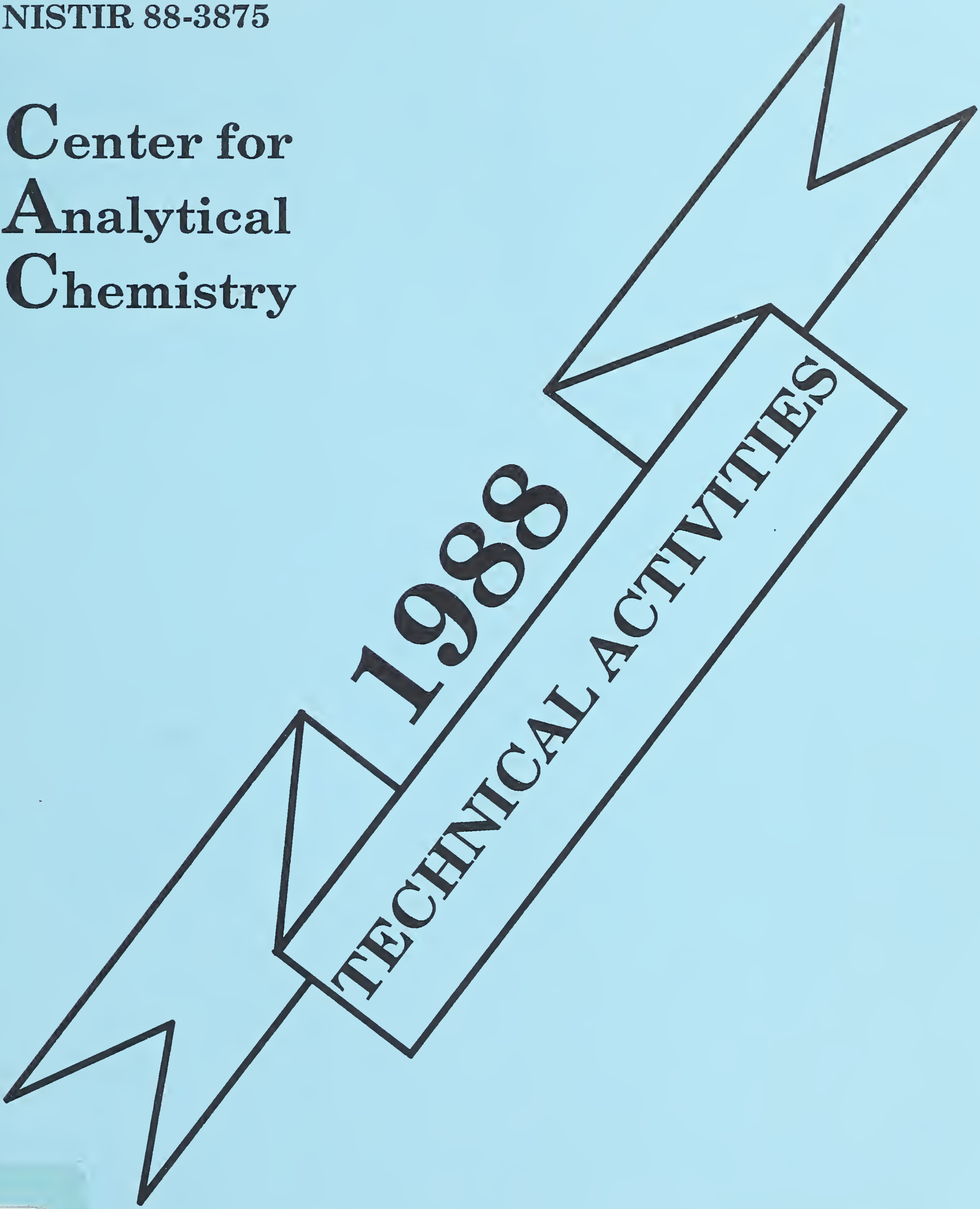
NISTIR 88-3875

Center for Analytical Chemistry



1988 TECHNICAL ACTIVITIES

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology

NISTIR 88-3875

Center for
Analytical
Chemistry

1988
Technical Activities

November 1988

Harry S. Hertz, Director
Center for Analytical Chemistry
National Measurement Laboratory

U.S. Department of Commerce, C. William Verity, Secretary
National Institute of Standards and Technology, Ernest Ambler, Director

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I. Center for Analytical Chemistry

Harry S. Hertz, Director
Richard A. Durst, Deputy Director (Acting)

A. Center Overview

The Center for Analytical Chemistry (CAC) develops and maintains the scientific competences and the experimental facilities necessary to provide the Nation with the basis for uniform measurements through development of measurement methodology and reference materials and provision of measurement services in the field of analytical chemistry. Analytical measurements provide a foundation for scientific and technological research and development concerning materials and their practical application. Analytical measurements are routinely used as a basis for regulatory decisions. Moreover, analytical measurements are increasingly used as the basis for industrial quality and health-related decisions. The Center serves as the National Reference Laboratory for assuring the reliability of analytical measurements.

The principal means by which the Center has served as a National Reference Laboratory is through the development of measurement concepts and methods, provision of quality assurance services, and certification of Standard Reference Materials (SRMs). The ubiquity of, and demand for, analytical measurements in modern society is reflected in the many SRMs produced in the Center. These reference materials are widely used in such diverse areas as the semiconductor and chemical industries, and in clinical and environmental laboratories. Each SRM is supported by research on homogeneity and stability and is certified as to chemical composition using the most reliable analytical methods available.

Analytical chemistry is increasingly being called upon to provide key data for highly complex sample types - high-technology materials, body fluids, plant and animal tissues, and foods. Increasingly, analytical values as a function of location within a sample are needed. As the demands upon analytical chemistry become more sophisticated, the problem of standardization becomes more challenging, both in terms of the number and the complexity of the needed measurement methods and reference materials. Since it is not reasonable to develop SRMs to deal with every measurement problem, the Center's program must be multifaceted and selective, seeking a variety of avenues to influence the quality of analytical measurements made in the United States. In addition to research publications and the certification of reference materials, the Center exerts influence through close contacts with various communities by means of workshops, symposia, and participation in professional societies and voluntary standards committees. Through such contacts, priorities are established for the development of measurement methods and the production of reference materials, and mechanisms are set in place for their effective use.

The expanded responsibilities which we have been given in becoming the National Institute of Standards and Technology, as reflected in our revised mission statement in the enabling legislation, provide a challenge for us to more directly couple with industrial needs in the United States and, in particular, to serve the metrology needs of emerging industrial technologies. A major component of industrial competitiveness is quality. With the emphasis currently being placed on quality at all levels of activity, the Center for Analytical

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NOTE: Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Chemistry has also been focussing attention on this issue. This has been accomplished through increased support of quality assurance functions in major national monitoring programs (such as the National Cancer Institute Chemoprevention studies and the NOAA Status and Trends Program), as well as through more carefully documenting our internal quality assurance practices.
This documentation, which is continuously updated and expanded has recently been combined with information on traceability of chemical measurements into a Center for Analytical Chemistry Quality Assurance Handbook. This document, in addition to being distributed to our own staff, has been made available to the analytical chemistry community. As a result, in the last several months, we have responded to over 800 requests for copies of the Handbook.

It is clear to us that the analytical laboratory is changing and will continue to change in the near future. Techniques we are developing and using today were unheard of several years ago. During the past year, we have implemented isotope dilution mass spectrometric procedures using combined LC/MS/MS and been able to demonstrate a relative precision of 1% for measurement of uric acid in serum. We have expanded our research efforts in the development of bioanalytical sensors, using liposome technology and flow injection immunoassays. With the installation of a cold neutron source in our research reactor, we are looking forward to significantly enhanced sensitivity in our ability to depth profile chemical concentrations of key elements in high technology materials utilizing a neutron beam, and to significantly enhance our ability for performing prompt gamma activation analysis. Characterization of large biomolecules (proteins and nucleic acids) is also receiving increasing attention with our enhanced capabilities for electrophoretic separations and digital imaging of two-dimensional electrophoreograms. Optimization of experimental design and of information utilization from multivariate chemical measurements is a focus of our growing effort in chemometrics. It is the intent of our research staff eventually to explore the total chemical measurement process.

One technique that is seeing a tremendous resurgence in CAC is wet chemistry. We are committed to renewing our capabilities in this area and to bringing this classical art into the 21st century. We have expanded our research base in laboratory robotics, to facilitate wet chemical separations. We are trying to capture the knowledge available so that wet chemistry can be applied to critical elemental assays and to the growing field of speciation, i.e., chemical analysis with retention of information on oxidation and binding states.

This year we were pleased to jointly dedicate with NIH, a new field emission scanning transmission electron microscope facility which has a one nanometer spacial resolution for analytical probes. We were also pleased this year to receive our seventh R&D 100 (formerly IR-100) Award since 1984. This track record clearly demonstrates the contributions that scientists in the Center for Analytical Chemistry are making to technology development. This year's award was for a newly designed conductance cell, which makes it possible to measure the cell constant directly, thereby improving the accuracy by a factor of 5 and establishing a better reference basis for conductivity measurements.

This past year also has included a notable increase in collaborative activities, through the sponsorship of research associates at NIST. The Motor Vehicle Manufacturers Association has sponsored a new research associate to improve reference technology and reference material availability for automobile emissions testing. The College of American Pathologists expanded its reference laboratory at NIST with the addition of a second research associate. These are two examples of our work to improve the accuracy base for chemical measurements on a collaborative basis.

In several weeks, we will cosponsor a conference at NIST with 13 professional, government, and industrial organizations on Clinical Laboratory Measurements: Accuracy and Patient Needs. This is a unique consensus building conference to look at accuracy issues associated with drugs of abuse, HIV (AIDS), cholesterol, and cytopathology (Pap) testing.

We are excited about our new ventures and look forward to playing an increasingly important and responsive role in setting a measurement accuracy base and in meeting the quality assurance needs of the American analytical chemistry community.

The programs of the Center strive to achieve a balance between the provision of currently needed reference materials and research efforts on new types of reference materials and methods of measurement. The work of the Center is performed in three divisions, each focusing upon specific analytes--inorganics, organics, and gases and particles. Within each division there are several groups representing separate analytical chemical disciplines, e.g, mass spectrometry and electrochemistry. Each division is responsible for a program in basic and applied research and maintains contacts with appropriate scientific and user communities.

In the following pages, some of the recent activities, technical directions, and outputs of the Divisions and groups are summarized.

B. Outputs and Interactions
(Center for Analytical Chemistry)

1. Publications

Hertz, H.S., Are Quality and Productivity Compatible in the Analytical Laboratory? Anal. Chem. 60, 75A-80A (1988).

Hertz, H.S., The How and Why of An Accuracy Base for Proficiency Testing Programs (with Michael J. Welch), Archives of Pathology and Laboratory Medicine 112, **343-345 (1988).**

Taylor, J.K., "Defining the Accuracy, Precision, and Confidence Limits of Sample Data," in Principles of Environmental Sampling, L. Keith, Ed., ACS Symposium Series No. 360 (1987).

Taylor, J.K., "Quality Assurance of Chemical Measurements," Lewis Publishers, Inc., Chelsea, MI 48118, 335 (1987).

Taylor, J.K., "How Good is your Data?," CHEMTECH, 74-77, March 1988.

Taylor, J.K., "Taking Relevant Samples," CHEMTECH, 294-296, May 1988.

Taylor, J.K., "Importance of Quality Assurance," Proceedings of the Accuracy in Trace Analysis Symposium, Journal of Research of the National Bureau of Standards, Vol. 93, Number 3, p. 232, May-June 1988.

Taylor, J.K., "Quality Control Data," Proceedings of the Ecological Quality Assurance Workshop, USEAP, Forest Response Program, Corvallis, Oregon 97333, September 1988.

Taylor, J.K., "Statistics in Chemical Measurement," MGI Management Institute, Harrison, NY 10528, 122, (1988).

2. Talks

Hertz, H.S., "The What, Why, and How of Future Chemical Measurements," International Conference on Laboratory Automation, Boston, MA, October 22, 1987. Invited

Hertz, H.S., "Quality Assurance, Reference Materials and the Role of a Reference Laboratory in Environmental Measurements, International Symposium on Trace Analysis in Environmental Samples and Standard Reference Materials, Honolulu, Hawaii, January 6, 1988. Invited

Hertz, H.S., "What is Accuracy," Media Workshop on Accuracy in Medical Testing, National Institutes of Health, Bethesda, M D, April 12, 1988.

Hertz, H.S., "An Overview of NCCLS," National Committee for Clinical Laboratory Standards Regional Meeting at the Gaithersburg Marriott, Gaithersburg, MD, April 26, 1988. Invited

Hertz, H.S., "An Overivew of NCCLS," NCCLS Executive Committee Meeting, New Orleans, LA, July 23, 1988. Invited

Taylor, J.K., "The Importance of Quality Assurance," Accuracy in Trace Analysis - Accomplishments, Goals, Challenges Symposium, NIST, Gaithersburg, MD, September 28-October 1, 1987.

Taylor, J.K., "Quality Control Data," Ecological Quality Assurance Workshop -USEPA, Denver, CO, March 30, 1988.

Taylor, J.K., "The Role of Statistics in Reference Material Measurements," 3rd International Symposium on Biological Reference Materials, Bayreuth, Germany, May 7, 1988.

Taylor, J.K., "Systematic Approach to Chemical Analysis," ACS Meeting, Toronto, Canada, June 6, 1988.

Taylor, J.K., "The Importance of Data Quality in Understanding and Controlling Emissions from Combustion Sources," ACS Meeting, Toronto, Canada, June 1988.

Taylor, J.K., "Assessing the Quality of Data," 30th Rocky Mountain Conference, Denver, CO, August 2, 1988.

3. Committee Assignments

Harry S. Hertz

Chairman, Education Committee, American Society for Mass Spectrometry
ASTM, Committee D19 on Water
ASTM, Committee E48 on Biotechnology
President, National Committee for Clinical Laboratory Standards
Analytical Laboratory Managers' Association
Department of Energy Health and Environmental Research Advisory Committee
FDA, Device Good Manufacturing Practice Advisory Committee

John K. Taylor

ISO/TC48, Glassware and Related Apparatus
ISO/TC48/SC01, Volumetric Glassware
ISO/TC146, Air Quality
ISO/TC146.01, Stationary Source Emission
ISO/TC146.02, Work Place Atmospheres
ISO/TC146.03, Ambient Atmospheres
ISO/TC146.04, General Aspects
ASTM D19.01, International Standards
ASTM D22, Sampling and Analysis of Atmospheres
ASTM D19, Water
ASTM D10.02, General Specifications and Technical Resources
ASTM D19.05, Inorganic Constituents in Water
ASTM D19.07, Sediments
ASTM D22.01, Quality Control
ASTM D22.02, Source Measurements
ASTM D22.03, Ambient Measurements
ASTM D22.04, Analysis of Work Space Atmospheres
ASTM D22.05, Indoor Atmospheres
ASTM D22.06, Acid Deposition
ASTM D22.09, ISO TAG for ISO/TC146

ASTM E34, Occupational Safety and Health
ASTM E36, Criteria for the Evaluation of Testing and/or Inspection Agencies
ASTM E36.10, Generic Criteria
ASTM E36.30, Nomenclature and Definitions
ASTM E41, Laboratory Apparatus
ASTM E41.01, Glass and Plastic Apparatus
ASTM E41.06, Weighing Devices
ASTM E41.07, Microchemical Apparatus
Collaborative Testing Subcommittee - Standard Methods
Advisory Committee - CHEMTECH (ACS)
ACS Committee on Environmental Chemistry - Subcommittee on Environmental Analytical Chemistry
Member, Editorial Board, AOAC

4. Sessions Chaired, Workshops and Conferences Organized

Harry S. Hertz

Symposium on Mass Education Introduction Lectures from Our Short Courses at the 36th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, June 3-10, 1988.

5. Center Colloquium Series

October 15, 1987

Sushma Palmer, National Academy of Science, Recommended Dietary Allowances Sciences

November 18, 1987

Haleem Issaq, Frederick Cancer Research Center, Analytical Chemistry in Cancer Research

February, 9 1987

John Bradley, McCrone Associates, Electron Microscopy of Interplanetary Dust

January 13, 1988

Devendra Lal, Scripps Institute, Terrestrial Cosmogenic Isotopes

March 19, 1988

Dale Schoeller, University of Chicago, Isotope Ratio Mass Spectrometery for Validating Dietary Intake

May 11, 1988

Peter Jurs, Pennsylvania State University, Prediction by Physiochemical Properties by Computer Methods

May 19, 1988

T.M. Thompson, NOAA Air Resources Laboratory, Trichlorofluoromethane (CFC11) and Dichlorodifluoromethane (CFC12) in the Western Pacific and Eastern Indian Oceans' Atmosphere and Surface Water

June 8, 1988

William Fateley, Kansas State University, Hadamard Transform Spectroscopy Analytical Application

September 28, 1988

William Betts, Supelco, Inc., Use of Class I Non-Specific Adsorbents for the Adsorption and Subsequent Thermal Desorption of Organic Contaminants in Air, Water, Soil, and Other Sample Matrices

C. Service Analysis

J.R. Moody and N.M. Crockett

The availability of Center for Analytical Chemistry analytical expertise to other institutions is an important service function. In addition to service analyses, CAC is frequently called upon to consult or advise, to provide various metrological calibrations of a chemical nature on a wide variety of industrial and research materials, and to provide analytical services of a unique nature such as compositional mapping, depth profiling, or ultra-trace analysis. These services are available to private industry when the uniqueness of the CAC capability has been demonstrated, and similar services are not available in the private sector.

All outside work is performed on a purchase order, while within NIST funds are obligated on an inter-division work order. The CAC staff is committed to providing the most timely, cost effective, and scientifically valid data possible. The time required varies upon such factors as size of the job and the availability of personnel. The simpler calibrations or analyses are typically completed in a few days to a few weeks. In all cases, work is performed on a cost reimbursable basis.

In FY88, CAC staff provided analyses or recalibrations for a total of 134 requests with a total reimbursable cost of $367,000. These requests and their associated funding were split among the three categories of customers as follows: NIST - 16 jobs ($108,700); other government agencies - 17 jobs ($129,000); and private industry - 101 jobs ($129,300). Requests for service work from private industry are now the largest category, reflecting a slow but steady growth in these requests. Overall, the dollar volume of service analytical and calibrations performed in FY88 are up about 23% from FY87.

II. Inorganic Analytical Research Division

James R. DeVoe, Chief
William F. Koch, Deputy Chief

A. Division Overview

The Inorganic Analytical Research Division conducts research that is directed toward improving the accuracy of compositional measurements of inorganic constituents in a variety of materials. This research takes the form of basic studies on potential new directions in chemical analysis as well as improvements to existing methods. In addition, the Division uses accurate methods to certify Standard Reference Materials, to provide analytical services for other government agencies, and to provide analytical support for solving problems related to national needs. The Division is organized into four Groups which are oriented to specific technical disciplines. The Groups are: Analytical Mass Spectrometry, Atomic and Molecular Spectrometry, Electroanalytical Research, and Nuclear Methods.

Our basic research program is directed toward the understanding of physico-chemical phenomena that will lead to an improvement in the accuracy of inorganic elemental analysis. This effort consumes some 5-10 percent of our budget and involves such studies as material transport of conducting solids by spark erosion, use of cold neutrons for nuclear methods of analysis, use of lasers in optical and mass spectroscopies, and the electrochemical properties of liquid junctions between half-cells. Out of our previous research efforts has come an important contribution to the measurement of conductance of electrolytes. A newly designed conductance cell makes it possible for the first time to measure directly the cell constant, thereby improving the accuracy by a factor of five. For this work we are pleased that Drs. Wu, Pratt and Koch have been awarded an R&D-100 award for 1988.

By far the largest effort, comprising approximately 60 percent of our budget, is the development of methods suitable for the accurate analysis of a variety of materials of interest to industry, other government agencies, and the Standard Reference Materials program. The paragraphs to follow discuss some of this effort in more detail.

This is the third year in our effort to regain lost expertise in wet chemical methods of analysis. We have now demonstrated a capability for both gravimetric and titrimetric methods. These methods have been selected to be complementary to existing capabilities. In addition, with contemporary methods of trace element analysis, we are in a position to measure the purity of separations by precipitation or extractions with a much higher degree of sensitivity than in the past. This should result in improvement in the accuracy of these methods. At the same time, we are exploring the possibility of automating some of these procedures to improve the reproducibility and to reduce tedium.

We have had a number of very important interactions and scientific exchanges with industry encompassing all facets of method development. For example, one of our staff spent six weeks at the Perkin-Elmer Corporation learning more about the coupling of instrument design with analytical applications and studying how accuracy in the measurements can be improved. We have a scientist from Eastman Kodak spending an extended period of time with us learning clean room sample processing and chemical separations for ICP-MS and OES. Over the years we have developed an unique expertise in the purification of acid reagents for sample dissolution. We are currently providing, for their evaluation, ultra-pure hydrofluoric acid to several chemical companies that produce analytical reagents. In addition, we have active collaborations with other companies to help them develop accurate methods of chemical analysis. These interactions are with the CEM Corporation on microwave methods of sample dissolution, Zymark Corporation on the use of laboratory robotics to prepare samples (chemical dissolution as well as separations) prior to instrumental analysis, Finnigan Mat on the evaluation of multi-element capabilities of thermal ionization mass spectrometry, and Dionex Corporation on the use of liquid chromatography for chemical separations. We have, for a number of years, had interactions with semi-conductor manufacturers, such as Intel, IBM, Eastman Kodak (EK) and Motorola, on trace elemental content using both trace element bulk analysis and neutron depth profiling (NDP). As a result of these efforts EK has provided funds for a new NDP instrument to be used with the cold neutron facility operated by the Nuclear Methods Group. Finally, under the auspices of the NCCLS we have a major program with eight instrument manufacturers of clinical potentiometric analyzers to improve accuracy in and to bring uniformity to the measurements of electrolytes in blood.

In view of the exponential growth in our capability to acquire and process information via desktop personal computers, whether it be quantitative analytical results or bibliographic data on analytical methods, we have explored the use of computer-based decision support systems to aid in the management of this information. Professor Frank A. Settle from Virginia Military Institute (VMI) has been with us this past year and has developed a prototype "expert system" that demonstrates an approach to handling analytical procedures using microwave heating of samples for dissolution.

Considerable effort has been placed within the Division on evaluating our methods development for the certification of Standard Reference Materials. Many of our studies have centered around the experimental design that includes all facets of the certification process. Out of these deliberations have come a number of ancillary studies such as a more detailed investigation of dissolution processes and possible elemental losses therein, the generation of proper conditions for establishing constant weight of samples to be analyzed along with possible elemental losses, and the establishment of valid methods to determine the homogeneity of concentration of the elements throughout the bulk of the material to be certified. In addition, when discrepancies between methods occur detailed experimental designs are generated at the Group Leader and Division Chief level to correct the source of error.

The remainder of our budget, approximately 20%, is devoted to the certification of Standard Reference Materials (SRMs). We have had a productive year in certifying SRMs with over 280 elements measured in more than 10 materials. As part of our commitment to improve the quality and expand the use of SRMs, we have instituted the policy of assigning a senior scientist within the Division as the technical focal point for the certification of a specific reference material. This "technical champion" is responsible for all technical and scientific aspects of the process from the sampling and collection of the material through the design of the certification to the interpretation of the results. This person is the primary contact on technical matters with the corresponding person in the Office of Standard Reference Materials. The first major material to be certified using this process is SRM 2704, Buffalo River Sediment, and from all indications this will be an outstanding reference material.

Our plans for new areas of research have been selected from a large number of excellent ideas generated by some of our most talented senior scientific staff. The number of projects is unfortunately constrained by our funding and available staff. Those projects that have been selected are the focussing of cold neutrons for the development of a neutron activation analysis microprobe, the applications of a UV-visible Fourier transform spectrometer, the thermodynamics of the sample dissolution process, and the use of ion sputtering in laser mass spectrometry. For method development, emphasis will continue on the use of "wet" chemistry, but using it in conjunction with the latest developments in instrumental methods. It is unfortunate that the universities have all but ceased adequate training in the wet chemistry area, and that analytical laboratories such as ours must take on this educational role. Considerable effort will be spent in the future on preliminary evaluation and validation of proposed reference materials at a much earlier time than is currently done. Validation includes most of the parameters which we have studied these past few years as indicated in the above paragraphs. Our staffing plans include replacement of senior staff where the need exists and adding new expertise in areas that we consider of new importance. In addition, we intend to hire more junior staff (e.g., at the BS level of education) to support our senior staff. This will lead to much better time utilization as well as potentially reducing the cost of analyses for the certification of SRMs.

This past year, we have established a pure reagents committee which has the responsibility for evaluating materials to be used as calibration standards and/or reagents for chemical processing. This committee will be responsible for obtaining the purest materials available and for the characterization of such materials. With increasing emphasis on the purity of materials and their stoichiometry, such as with super- and semi-conductors, we intend to be the focal point for the purest available materials.

1. Analytical Mass Spectrometry Group: Overview

The Analytical Mass Spectrometry Group performs compositional measurements using the analytical sciences of chemical separation and mass spectrometry. For many years, the Group has been involved in making isotope ratio measurements with the highest precision and accuracy. These measurements are done using thermal ionization mass spectrometry on highly purified elemental materials. The separation of elemental species, often from very complex matrices, with high efficiency and low contamination, is an expertise that is required to complement the capabilities of thermal ionization mass spectrometry for making precise and accurate isotope ratio measurements. The Group has applied these measurements to the determination of the atomic weights of the elements and chemical analysis by the technique of isotope dilution. While maintaining the basic thrust in the traditional areas, the horizons of the Group have broadened markedly in recent years. New techniques in sample handling and preparation, separations, and mass spectrometry have been introduced.

An inductively coupled plasma mass spectrometer (ICP-MS) has been in operation in the Group since 1985. This instrument is becoming one of the most popular new analytical tools for elemental determination because of its high sensitivity, direct sample introduction, and broad elemental coverage. It has been applied to a variety of programs within the Group. The ICP-MS has replaced the spark source mass spectrometer as the method of choice for the characterization of high-purity reagents that are produced in the Group. The sensitivity of ICP-MS is higher for all elements, some by an order of magnitude and more; sample throughput is dramatically improved; and, the total number of elements quantified is almost double (37 versus 19). Isotope dilution analysis has been done for SRM certification which required no chemical separations. The best isotope ratio precisions to date have been made in the calibration of standard solutions, approximately 0.25%. The instrument has been used in concert with liquid chromatography as a species-specific element detector and mercury compounds have been quantified in a variety of materials. Also, the ICP-MS is being applied to determine trace Nd in a number of materials, including La, as part of a program to produce efficient optical fibers. The development of procedures to separate Nd from La is required in this project and the ICP-MS has been used interactively in developing this difficult separation as well as for the ultimate analysis.

High precision thermal ionization mass spectrometry (TIMS) is now done in the Group using the traditional NBS-built instruments and a multicollector, fully automated commercial instrument. The redetermination of the atomic weight of nickel is essentially complete, except for the statistical analysis of the data. This work was done on both types of instruments and a comparison of the results is of considerable interest. The ratio measurement precisions of a few parts in 10^5 will result in an atomic weight determination improved by a factor of 10-100. The multicollector TIMS instrument has also been applied to other programs of high precision isotope ratio measurement, including Nd tracer work and isotope dilution analysis of lead in a new series of fuel SRMs. The instrument has demonstrated parts-per-million internal precisions. Procedures have been developed for the high precision isotopic measurement of both boron and lithium, which will allow the more accurate measurement of these elements by isotope dilution. In the past, measurement precisions for these elements have been poor because of the relatively large mass difference between the isotopes. In the last year, an effort has begun to develop multielement isotope dilution TIMS procedures. We hope this effort will make isotope dilution more generally applicable and economically competitive by increasing analytical throughput, while maintaining the highest precision and accuracy. The Group has made significant contributions to the certification of various Standard Reference Materials by TIMS in the past year, especially for the determination of sulfur.

The laser resonance ionization mass spectrometry (RIMS) program has continued, primarily on the basis of interactions and collaborations with scientists both within and outside National Institute of Standards and Technology (NIST). The NIST program was highlighted at the 4th International Symposium on Resonance Ionization Spectroscopy (RIS), which was held at Gaithersburg in April 1988. The unique application of RIMS to Os/Re problems in isotope geology has created much excitement and a demand for instrumentation. The Group has helped in the building of a RIMS instrument at the Carnegie Institute of Washington. RIMS is also being applied to the analysis of high purity semiconductor devices. Vanadium has been chosen to demonstrate the selectivity of the resonance ionization process; interferences by chromium and titanium make mass spectrometric measurement of vanadium at ultratrace levels extremely difficult.

The Group has designed and built several pieces of analytical instrumentation in the past year. A state-of-the-art magnet controller is presently being evaluated. A filament degas vacuum system has been redesigned and built. It promises faster and more reliable preparation of sample filaments. The Group has provided a duplicate of this system and built a quantity of other NIST-designed electronic components, including the IR-100 award winning parametric amplifier, as a service to academic, governmental, and industrial organizations. The Group designed and built a high-capacity still this year, which initially has been used to produce ultrapure hydrofluoric acid. This acid is absolutely essential in the preparation and analysis of several high technology materials, including optical fibers and semiconductors.

In the future, the general research program of the Analytical Mass Spectrometry Group will continue to be directed toward goals of improving sensitivity, applicability, precision and accuracy of isotopic ratio measurements. The program will continue to encompass state-of-the-art instrumentation and emerging ideas and concerns in inorganic analysis. The use of isotopic tracers in environmental and other studies will certainly play a major role in the activities of the Group. An anticipated continuation of the feasibility study that was done for the Electric Power Research Institute on the use of rare earth isotopes as tracers of power plant emissions is one example of our activity in this area. The development of new atomization techniques in laser mass spectrometry and the measurement of radioactivity by mass spectrometry are both areas with potential for the future.

Jack D. Fassett, Group Leader; I. Lynus Barnes, Ellyn S. Beary, William A. Bowman, III, Diane S. Bushee, Emile C. Joel, John W. Gramlich, W. Robert Kelly, George M. Lambert, John R. Moody, Thomas J. Murphy, Paul J. Paulsen, Liu Qi, Ronald W. Shideler, Richard J. Walker, and Xiao Yingkai.

2. Atomic and Molecular Spectrometry Group: Overview

The Atomic and Molecular Spectrometry Group investigates fundamental processes in atomic and molecular spectroscopies to develop new analytical techniques and to improve existing analytical methodology. Research and development activities include areas of atomic emission, absorption, and fluorescence spectrometry, as well as resonance ionization mass spectrometry (RIMS), and the application of laser enhanced ionization (LEI) processes in flames and photoionization processes in mass spectrometry. The developmental research emphasizes the detection of all random and systematic errors and applying these resulting methodologies to the certification of Standard Reference Materials (SRMs).

LEI spectrometry has proven to be a very sensitive method for determining certain trace elements. Complex matrices have been analyzed accurately by incorporating chemical separations prior to the instrumental measurement step. Separations are necessary because background levels, line shapes, and noise are related to the presence of easily ionized species in the flame. Research on the fundamental processes of laser excitation and ionization has been undertaken with the development of an instrumental system for simultaneous LEI and laser induced fluorescence (LIF) measurements in the flame. This capability is being used to characterize and correlate noise sources, as well as to investigate excitation wavelength profiles. Understanding these phenomena is crucial to dealing with interferences caused by easily ionizable elements in analytical samples. Other methods for reducing the effects of elemental interferences have been developed including the use of liquid chromatography (LC) with LEI spectrometry. Tributyltin (TBT) has been successfully separated from dissolved samples of marine sediment using LC. LEI has then been used as a tin-selective detector with a detection limit of 9 ng Sn/g sediment.

A number of analytical methods are being investigated which involve direct sampling of the solid material to be analyzed. The goal of this research is to improve sensitivity by eliminating the dilution of analyte inherent in the chemical dissolution step and to improve accuracy by avoiding analyte losses due to incomplete dissolution of complex samples. LIF has been used to examine the direct solid sampling characteristics of a commercial glow discharge sputtering source. Back-scattered fluorescence has been detected for Fe in a copper matrix, but further refinements in the collection optics are still necessary to realize our goal of ppb detection limits in the solid. Direct solid sampling also has been investigated to improve the sensitivity of trace contaminant detection in silicon-based glasses using atomic absorption spectrometry (AAS) with Zeeman effect background correction. Direct injection of the solid powder with the appropriate matrix modifier allows in-situ digestion and quantitation of trace elements using aqueous standards. For SRM 614, Trace Elements in Glass, Co, Cu, Fe, and Ni were found to be within the certified range for these elements. The analysis of aluminum- and zirconium-based glass matrices is also being investigated. A related technique of slurry sample introduction also has been developed to assess the homogeneity of sediment Standard Reference Materials. This approach allows a rapid means of monitoring the blending process for a candidate SRM and for determining its sampling constant.

The attainment of accuracies and precisions to better than 0.2% relative for major and minor constituents is another active area of research and methods development in the Group. Methods for measuring the stoichiometry of superconducting materials have been devised using inductively coupled plasma (ICP) spectrometry. Stoichiometry is measured in a highly precise and accurate mode of analysis using simultaneous internal standardization to reduce correlated noise. The principal advantage of the ICP approach is its speed and overall uncertainty of less than 0.5% relative for the elements Cu and Y in Ba-Y-Cu-O superconducting compounds. Detection of trace element contaminants in these materials is also accomplished in a survey sequential mode of analysis that checks for the presence of 36 elements.

The continued development of integrated techniques involving both instrumental spectrometry and classical chemical analysis has enabled the Group to determine major and minor constituents in geological materials with high accuracy and precision. Analysis of filtrates and redissolved precipitates has significantly decreased the number of chemical separation steps required to correct for interferences in gravimetric analyses. This effort has also included the utilization of automated titrimetry, automated separation methods, and microwave dissolution techniques to improve the accuracy and to shorten the time required to complete the analyses.

Homogeneity testing and analysis for certification of SRMs continue to be principal activities in the Group. This year, approximately 100 elements in over 75 materials were determined. Calibration studies have focussed on the need for more accurate values for boron in a number of low alloy steel SRMs to be used by spark emission spectrometry. Sixty-three single element spectrometric calibration solution SRMs have been produced, and a number of other SRMs, including bovine serum, oyster tissue, total diet, and apple and peach leaves were analyzed by a variety of methods in the Group. Optical filter absorbance SRMs continue to be certified and special calibrations of other optical filters have been completed for customers. The process of certifying elements in the candidate Buffalo River Sediment SRM was completed this year. This effort began three years ago by one of the Group members, who designed and coordinated the entire certification process including both NIST and outside laboratory analysis activities.

Materials also have been analyzed for other government agencies. For example, the correlation between material failure and chemical composition of machine bolts has been carried out in cooperation with the NIST Institute for Materials Science and Engineering. Welds and baseplates from the collapsed oil tank in Pennsylvania were examined using spark optical emission spectrometry. Participation in round-robin studies has continued in support of a National Cancer Institute study of Ca, Se and Zn in blood, and Al has been determined by atomic absorption spectrometry in a Food and Drug Administration serum albumin reference material.

The effort to update and automate analytical instrumentation in the Group has continued with the modification of the high-accuracy optical filter spectrophotometer system and the acquisition of a computer-controlled microwave oven for sample dissolution. The Group continues to benefit from programming and computer application expertise which leads to both precise and accurate control of instrumental systems, as well as complete statistical analysis of data.

The Group has maintained its high level of cooperative research with NIST and visiting scientists. For example, we have worked with Joseph Bodkin at the Mineral Constitution Laboratory of Pennsylvania State University to become familiar with classical methods of analyses. Mr. Bodkin has also worked in the NIST laboratories continuing the development of gravimetric and titrimetric analyses. Dr. Michael S. Epstein has spent six weeks working in the product development laboratory of Perkin-Elmer Corporation to study the application of new commercial atomic spectrometric instrumentation for high accuracy analysis of SRMs and the slurry sample introduction for AAS homogeneity assessment. A number of foreign guest scientists continue to work in our laboratories investigating methods of analysis of pure reagents and compounds. Dr. Radu Mavrodineanu returns to the Group periodically to consult on the calibration of optical absorbance filters. This consultation has assisted us in maintaining our high-accuracy absorbance measurement capabilities since Dr. Robert W. Burke retired from the Group.

In the future, the Group plans to continue applying laser techniques to the accurate analysis of SRMs, using chemical separations to reduce or eliminate matrix effects. We will pursue LIF in the glow discharge sputtering device, as well as investigate opportunities for determining C, N, and P using multiphoton ionization. Both Nd-YAG and diode lasers will be used to probe the glow discharge as a source of atomic vapor for spectrometric analysis, and work will continue on LIF and LEI in a power-modulated ICP. There will be an increase in focus on the accuracy of dissolution methods. Incomplete dissolution and losses of volatile elements will be examined. Several methods including neutron activation analysis, available in the Nuclear Methods Group, will be used to detect such phenomena. Group chemical separations will continue to be examined to provide both spectrometric techniques and classical methods with matrix interference-free samples for analysis. A new area of research in ultra-high resolution spectroscopy using Fourier transform spectrometry will be instituted in the Group. Accurate spectral line identification and unambiguous characterization of line interferences will be among the goals of this effort.

Robert L. Watters, Jr., Group Leader; Therese A. Butler, Alissa M. Conklin, Nicole M. Eaton, Katherine S. Epler, Michael S. Epstein, Roger T. Fang, Robert C. Gauer, Radu Mavrodineanu, John A. Norris, Theodore C. Rains, Fillmer C. Ruegg, Theresa A. Rush, Francis H. Shen, Johanna M. Smeller, Melody V. Smith, John C. Travis, Gregory C. Turk, Thomas W. Vetter, H.S. Wang, Laura J. Wood, and Z. Xu.

3. Electroanalytical Research Group: Overview

The Electroanalytical Research Group conducts basic research and utilizes electrochemical principles and chromatographic separations to develop new techniques, to improve existing techniques, and to apply them to chemical analyses. The techniques in practice include amperometry, chelation chromatography, conductimetry, coulometry, ion chromatography, polarography, potentiometry, robotics, supercritical fluid chromatography, titrimetry and voltammetry. Research activities are directed toward attaining a more thorough understanding of electrochemical systems, thermodynamics and exchange mechanisms encountered in the development and implementation of electroanalytical and separation methods.

The Electroanalytical Research Group continues to expand its resources and scope of research through a number of professional collaborations such as the Research Associate Program (RAP), and by utilizing guest scientists from both industry and universities. In addition, the Group maintains its involvement with ASTM, the American Water Works Association (AWWA), the International Union of Pure and Applied Chemistry (IUPAC), and the National Committee for Clinical Laboratory Standards (NCCLS).

There are three RAP projects in the Group. A research program with CEM Corporation, a producer of microwave equipment for research purposes, has the goal of developing techniques for the dissolution of samples in closed vessels within a microwave heating chamber. A second RAP is sponsored by the NCCLS and is funded by a consortium of eight manufacturers of potentiometric analyzers for clinical applications. The purpose of this project is to develop reference materials and methodology for measuring the activity of free ionized sodium, potassium, and calcium in serum with ion-selective electrodes. The third RAP is with the Dionex Corporation to develop ion chromatographic separations of the transition metals. The applicability of chelating resins to ion chromatography is being investigated and has led to the development of a new procedure for which a joint patent application with the Dionex Corporation has been submitted.

Progress is being made in electrolyte theory with the help of a number of noted experts such as Harold Friedman (State University of New York at Stony Brook), Walter Hamer (NIST retired), Vincent Bower (NIST retired), Rabindra Roy (Prof. of Chemistry, Drury College), Robert Wood (Prof. of Chemistry, U. Delaware), Robert Kay (Prof. of Chemistry, Carnegie-Mellon Inst.), and Arthur Covington (Prof. of Chemistry, U. of Newcastle-Upon-Tyne, GB). The plan to improve the state of pH measurements and standards may ultimately lead to a single, unified pH scale. The problem of standardizing high ionic strength pH measurements has been approached in two ways. First, with the help of several guest scientists including Feng Daming, a guest scientist from Guangzhou Research Institute of Non-ferrous Metals, Peoples Republic of China, Prof. R. Roy and P. Lord, Drury College, studies have been initiated to better understand and characterize the liquid junction potential. A flowing liquid junction cell has been designed that has a highly reproducible and predictable liquid junction potential. Second, the thermodynamics and transport phenomena of multi-component systems have been explored using the cross-square rule which is a theory describing ion-ion interactions. A paper has been prepared describing these investigations. To aid in the measurement of pH in physiological solutions, such as serum, a zwitterionic buffer (HEPES/HEPESATE) has been certified as a pH Standard Reference Material. This SRM is the first pH standard with certified values given at an ionic strength of 0.15, similar to that found in serum.

Work has been completed, in collaboration with Division 553, on the automation of the separation of the transition elements from the alkali and alkaline earths for biological samples that are to be analyzed by X-ray fluorescence. In addition, a study has been initiated on the applicability of supercritical fluid chromatography and reversed-phase HPLC for metal separations. Ion chromatography has been extensively used for determining sulfur and chloride in a variety of SRMs (coals, oils, oyster tissue, total diet). Two new Anion Standard Solutions (nitrate and phosphate) at concentrations of 1000 g/g have been tested and shown to be stable for at least one year. Fluoride in timothy grass and oyster tissue has been determined using oxygen bomb combustion, followed by ion-selective electrode potentiometry.

Research is continuing in the development of aqueous electrolytic conductance standards. A novel conductance cell using a variable, but accurately known cell length, has been designed and implemented. This approach has resulted in an absolute measure of the cell constant and has confirmed and improved the accuracy by a factor of five for the secondary standard, as recommended by the International Organization of Legal Metrology (OIML) for the specific conductance of aqueous solutions of KCl. Drs. Wu, Pratt and Koch have received an R&D-100 Award for this unique cell design. Two new Standard Reference Materials have been produced and certified with this new system.

This year there have been a number of new procedures for dissolving samples by microwave heating. For example, methods have been developed to replace current EPA procedures for the dissolution of solids in water, oil, soil, and sediments. These procedures will result in considerable time savings as well as improving the accuracy of the analyses. The first reference book on microwave-assisted sample preparation has been completed. It contains fundamental theory and reference data for predicting temperature conditions from estimates of input power. A very sensitive electrochemical means of determining if trace organics or metal-bound organics remain after microwave-assisted sample digestion has been developed .

The project to investigate the utility of robotics for laboratory use is well underway with the successful demonstration of a chelation separation of metals under computer-assisted robotic control. Work this year has concentrated on upgrading the hardware and software needed to improve reliability. The system was used to separate a number of transition elements for several SRMs, such as the river sediment, mixed diet, and orchard leaves which are currently in the process of certification.

Dr. Frank A. Settle from Virginia Military Institute has completed a sabbatical at NIST. Using a commercial "shell" type of expert-system software, he has completed a prototype system to assist the analyst in selecting appropriate conditions and thereafter to set up and control microwave equipment for acid decomposition of samples. This work is believed to be the forerunner of software which will aid the analyst in selecting proper conditions for performing a variety of chemical analyses.

Of particular significance was the preparation and certification of a frozen bovine serum SRM (1598) under the technical guidance of Dr. H.M. Kingston. This SRM, a cooperative effort with USDA, has several elements certified at the lowest concentrations in any standard material of this type.

Research in pH will continue as a long-term commitment to provide reliable and thermodynamically significant measurements and standards. The development of a series of matrix-specific pH standards is a high priority. The group plans to prepare and certify additional zwitterionic pH Standard Reference Materials for use in physiological pH measurements. Investigations in aqueous conductance will continue in collaboration with the Hungarian Office of Measures.

An important research direction for the Group is, and will continue to be, in the area of separations science. Most, if not all, instrumental techniques can perform at their optimum sensitivity, selectivity and accuracy only if sample matrices identical in nature to the calibration standards are used. The goal of this separations research will be to develop the means of providing such samples through the exclusion of interfering metals, the removal of major constituents, and the preconcentration of trace metals. Speciation of the metals by valence and complexation may also be possible. Novel chelating resins are in the developmental stages and will be applied in conjunction with ion chromatographic separations. The direct combination of chelation chromatography with spectroscopic instrumentation is being evaluated.

Advances in ion chromatography will be explored to lower the detection limit and expand its applicability to new elemental species. Flow-injection analysis with electrochemical detection will be implemented for the determination of ultra-trace metals in complex matrices. Voltammetry will be used extensively as a valuable analytical research technique in metal determination and speciation.

Expert systems coupled to automated equipment and robots can provide the flexibility required to achieve fully automated procedures for sample preparation. Research in the use of laboratory robotics for microwave-assisted acid decomposition has been initiated. A demonstration project has been started to adapt a commercial shell expert system to address the needs of analytical chemists and to assist them in selecting the best method of decomposition from an ensemble of procedures. Ultimately, this expert system will drive the laboratory robot.

Howard M. Kingston, Acting Group Leader; Jeffrey H. Barr, Zou Chun, Courtney A. Clements, Feng Daming, Xie Guirong, P. Chandrani Gunaratna, Lisa A. Holland, Lois B. Jassie, William F. Koch, Pamela J. Lord, George Marinenko, Margo D. Palmieri, Kenneth W. Pratt, Rabindra Roy, Frank A. Settle, Archava Siriraks, Peter J. Walter, and Yung Chi Wu.

4. Nuclear Methods Group: Overview

The development and application of nuclear analytical techniques for greater accuracy, higher sensitivity and better selectivity are the goals of the Nuclear Methods Group. A high level of competence has been developed in reactor-based activation analysis, which includes instrumental and radiochemical neutron activation analysis (INAA and RNAA). In addition, the group has a unique capability in neutron beam analysis with both prompt gamma activation analysis (PGAA) and neutron depth profiling (NDP). The NDP technique utilizes prompt charged particle emission to determine elemental distributions within the first few micrometers of a surface, while the PGAA technique utilizes prompt gamma-ray emission to measure the total amount of an element in a sample regardless of its distribution. These techniques provide an arsenal of tools to address a wide variety of analytical problems in science and technology.

The activities of the past year have been highlighted by the initiation of the National Facility for Cold Neutron Research to be established at the National Institute of Standards and Technology (NIST) during FY89. The Group's involvement includes the design and construction of second generation instruments for PGAA and NDP. During FY88, the cold source was installed and became operational, and construction of the guide hall will be completed during the first quarter of FY89. The Group's efforts have been aided substantially by its ability to use the existing cold neutron beams at the KFA Jülich (West Germany) facility. Plans are underway to include both the PGAA and NDP experimental systems in the first phase of implementation. A major grant from the Eastman Kodak Company is contributing to the timely development of NDP using cold neutrons.

The Group's contribution to the certification of Standard Reference Materials is illustrated by the multielement measurements done on the SRM Bovine Serum, Buffalo River Sediment, and glass-film XRF standards. Work has been initiated on the new Orchard Leaves, Total Diet, Oyster Tissue, and a carbonaceous marine sediment, with Group members serving as the Technical Champions on each of these new SRMs. A new ability to quantify nitrogen in biological samples has resulted from this year's research to develop a NAA liquid-scintillation beta-counting method exploiting the thermal neutron reaction $^{14}N(n,p)^{14}C$ and measuring the radioactive CO_2. This project is being done in collaboration with the University of Illinois.

The Group has taken an active role in the NIST's program on high-temperature superconductivity, both in the measurement of impurities in starting materials and in final products, and in the determination of the actual stoichiometry of the metallic constituents. The effort this year has been in the development of accurate, rapid measurements of these materials by both NAA and PGAA.

The Biomonitoring Specimen Bank Research Project continued its support for other agencies' monitoring programs. These included the EPA human liver project, the NOAA National Status and Trends program, the NCI Micronutrient program, the IAEA/FDA/USDA Total Diet Study, and most recently, the NOAA Alaska Marine Mammal Project. Research has centered on developing protocols and improved analytical methodology. Our participation in intercalibration exercises with the project participants and the development of marine QA materials helped to enhance the quality of the analytical results used in the assessment of the Nation's environmental health. Of major importance this year has been the completion of the re-analysis of 30 livers each, from the 1982 and 1984 collections, to quantify the stability of key elements under the carefully controlled storage conditions.

Bioanalytical research focused on the determination of metal species in various materials. Elements at trace and ultratrace levels have been determined in separated proteins and other macromolecules. The use of autoradiography to determine selenium has been added to the INAA and RNAA techniques. The occurrence of inorganic and organic compounds of tin in marine tissues is also being studied.

The strong interactions with industrial scientists using NDP, PGAA, and NAA has continued with a growing number of guest workers, research associates, and joint publications. An important development this year has been the demonstration of two-parameter, coincidence spectroscopy for thin samples in collaboration with the group under Professor W.-K. Chu at the University of North Carolina and with Scientists at the Eastman Kodak Company. For appropriate samples, this technique will increase the measurement sensitivity equivalent to a ten-fold increase in reactor neutron flux. The measurement of distributions of lithium and boron in metals, glasses, and polymers continues to produce important results.

The joint NIST/FDA/USDA study of trace elements in human diet, sponsored by the International Atomic Energy Agency, has completed its fourth year. A total of 40 minor and trace elements have been measured on the U.S. total diet material collected from several regions. In addition, measurements have been carried out on selected elements in diets received from countries participating in this global study. A candidate total diet material prepared in cooperation with OSRM is being evaluated as an elemental standard.

Special emphasis will be given to the completion of the initial phases of the design of the cold neutron NDP and PGAA systems. In addition, a facility is envisioned at which we will study the technique for focusing neutron beams onto a small area thereby increasing the neutron intensity, with the ultimate goal of generating an activation analysis milli- or microprobe.

Particular attention will be paid to count rate dependent effects, gamma-ray self-absorption, detector efficiency calibration, and monitor activation analysis. Maintaining full accuracy at high count rates using current-generation data-acquisition electronics is the goal of our count rate dependent studies. Accurate quantification of gamma-ray self-absorption and measurement of the shape of the efficiency curve are required for accuracy in monitor activation analysis since matching of sample with primary standards is not done. The development of monitor activation analysis is part of the high-temperature superconductivity effort to achieve rapid sample turnaround with minimum sacrifice of accuracy; however, the approach will also provide good quality control when used in parallel with traditional primary standard NAA.

Ronald F. Fleming, Group Leader; M. James Blackman, Donald A. Becker, David M. Byron, R. Gregory Downing, Kathleen A. Fitzpatrick, Brent L. Grazman, Robert R. Greenberg, G. Venkatesh Iyengar, John K. Langland, Richard M. Lindstrom, J. Emlen Meyers, Eline R. Myklebust, Bruce R. Norman, Craig A. Stone, Susan F. Stone, Theresa M. Sullivan, Dana K. Weiss, and Rolf L. Zeisler.

B. Selected Technical Reports
(Inorganic Analytical Research Division)

1. Development of Ion Chromatographic Methods for the Determination of Transition Metals Using Chelating Resins

A. Siriraks and H.M. Kingston

A new procedure has been developed for coupling chelator chromatography to ion chromatography. The procedure involves introducing a sample, altering the matrix and integrating the chelation chromatography into an ion chromatograph. The process allows the elements of interest to be concentrated and separated from other groups of elements and matrix components that would prevent the use of ion chromatographic procedures. The equipment configurations and processes makes possible the use of ion chromatographic analysis for transition elements in many sample categories that could not be analyzed by simple ion chromatographic procedures for transition metals. This research has led to a joint patent application between NIST and the Dionex Corporation.

Materials that must be analyzed for trace elements are usually the least compatible with the ion chromatograph. Because of the natural distribution of elements in real materials, the matrix contains large amounts of salts as compared to the transition and rare earth elements. This concentration difference can be from one thousand to one million times greater than the trace transition elements of interest. Ion chromatography is not used for these common samples but is limited to aqueous samples with salt concentrations only a few times higher or equal to that of the elements of interest. Using conventional ion chromatography, these problems prevent many samples from being analyzed (biological, botanical, geological, and environmental).

With this new method, an iminodiacetate chelating resin is packed in a plastic high pressure (2000 psi) column and placed before the concentrator column. The alkali and alkaline earth elements are removed and the counter ion replaced with the ammonium ion. Tests with the traditional chelation resins proved incompatible and they were replaced by a highly cross-linked iminodiacetate resin to provide stability under pressure.

New conditions were developed to perform chelation chromatography. The chelator column was used to preconcentrate and preseparate high salt containing samples. The column was then stripped of its remaining elements and a method of placing these ions directly onto the concentrator column was developed. This procedure required precise control of pH, flow rate, reagent mixing, and ion concentration. Column capacity matching was used to control the availability of competing ions and the removal of the metal from the concentrator column. A procedure of controlled reverse flow for removal of the ions from the concentrator column was used to recombine and compress the element band prior to its entry onto the analytical column. At this point classical ion chromatographic separation procedures and post-column derivatization are possible for element detection. These procedures have previously been limited to samples containing no interfering salts. The procedure requires less than one hour for each sample being analyzed for a group of elements.

The applications for this procedure are divided into several categories. The most obvious is a new type of chromatography identified as ChIC for Chelation Ion Chromatography. Its uses include the direct analysis of trace transition metals in a wide variety of real samples. In general, acid-decomposed biological, botanical, geological and environmental samples are appropriate sample matrices for trace transition and rare earth element analysis. The elements that can be analyzed are those that can be retained by the chelating resin. Different elements may require totally different detection systems. Seawater and digested animal tissues have already been tested for this application. The technique has been used to quantify six elements in sea water at the 1-5 ppb level and three elements in oyster tissue at the 20-800 ppm level. ChIC can also be used as a separation system for another analytical instrument that performs the element detection and quantification. This can be done in two different modes. The first is in a batch mode, where the separated element or group of elements from the chromatographic instrument is collected in a beaker. This becomes the sample in a modified matrix on which another analytical instrument performs analysis. The second is the direct coupling of the chromatographic instrument to another analytical instrument to retrieve the element or group of elements from the chromatographic stream. The chelator column can be used alone to produce a group separation and thereby to provide on-line separations whose products can be introduced into other analytical instruments, thus, increasing sensitivity and removing interfering elements.

2. Interlaboratory Test Studies for the Development of Reference Materials for Potentiometric Sodium and Potassium Measurements in Human Serum

W. F. Koch, P. C. Gunaratna, and R. C. Paule

Ion selective electrodes (ISEs) have gained widespread acceptance as the method of choice for measuring electrolyte concentrations in biological fluids. Since such measurements can be performed in undiluted specimens, the measurements can be made with less sample preparation, and hence tend to be faster and more reliable. The required instrumentation for ISE determinations is less complicated than flame photometers, and generally less training is required to operate ISE apparatus on a routine basis than that for flame measurements. Furthermore, because ISEs respond to the ionic activity rather than to the concentration, the measurements may be physiologically more relevant, at least in the ideal. However, the theory necessary to determine electrolyte activity accurately in biological fluids has yet to be developed.

Because of the historical acceptance of flame photometric values for electrolytes (especially for sodium and potassium) in biological fluids, it is desirable that the values obtained by ISEs in undiluted specimens be consistent with the flame values. This avoids complications in defining different reference ranges and minimizes confusion and possible errors in diagnosis and treatment. However, as alluded to above, there are fundamental differences in the measurements, which make consistency in the reported values more a matter of convention than of hard science. In brief, the flame method (and to a certain extent, ISE measurements in diluted samples) measures total concentration of a given electrolyte (e.g., sodium) in a given volume of solution. On the other hand, the ISE method applied to undiluted specimens responds to the thermodynamic activity of free sodium ion in the volume of solvent, not the total volume of solution. Protein-bound electrolyte is not sensed by an ISE. Furthermore, the ISE method is subject to biases due to residual liquid junction potentials and protein effects at the electrode. Thus, calibration of the ISE method according to a strict protocol and with well-designed reference materials is critically necessary to bring conformity and consistency to ISE measurements. An accurate calibration solution should simulate the actual sample, to minimize the effects of liquid junction, activity, protein volume and other factors which affect the electrode potential.

The objective of our present study, funded by the instrument manufacturers through the National Committee for Clinical Laboratory Standards, is to develop suitable reference materials and to certify them for the concentrations of Na^+ and K^+. As part of this study, a four-stage interlaboratory test has been carried out. Eight instrument manufacturers and three independent hospital laboratories participated in these tests. The primary purpose of the initial interlaboratory test was to check the test protocol. The second interlaboratory test was designed to find a suitable material which could minimize the deviation between laboratories. The purpose of the third interlaboratory test was to test the linearity of the ISE measurements and the performance of the material selected in the second round robin. The fourth test was intended to test a prototype reference material, and is still in progress.

As. If standards can be prepared to closely match sample matrix, such as a standard reference material (SRM), calibration of the ETAAS instrument is not a major problem. But SRMs matrices are limited and the analyst has resorted to the standard addition method. Standard addition has long been considered as an effective way to combat the multiplicative interferences in aqueous samples. The application of standard addition is based on the assumption that the analyte added is in the same chemical form as in the unknown sample. Usually this is not the case in solid samples.

The data for sera which had been lyophilized and then reconstituted have indicated that these materials do not perform well as calibrants for ISE measurements. However, the development of Standard Reference Materials made of frozen human sera should be feasible. Such materials should help individual laboratories make more precise ISE measurements for both Na^+ and K^+.

3. Establishment of Absolute Values for the Specific Conductance of Aqueous Solutions of Potassium Chloride for Improved Measurement Accuracy

Y.C. Wu, K.W. Pratt and W.F. Koch

Electrolyte conductance is an important property of electrolyte solutions. The specific conductance κ, Siemens per centimeter, S cm^{-1}, is determined by the ratio G/R, where the cell constant G is the ratio of the effective length l to the electrode area a (i.e., l/a), and R is the resistance of the solution contained in the cell. Generally, R can be determined to the desired degree of accuracy. If G is known, κ can then be determined. On the other hand, one can use a material of known κ, such as mercury, to determine the cell constant G, from which the κ of other solutions can be measured. The latter is the basis for the determination of the conductivity standard for KCl solutions that have been used for the past 50 years.

After reviewing these standards, with the necessary corrections for the changes in the values of the basic units, viz., the ohm; the temperature scale; and the volume unit, the corrected values differ numerically from the originals. Moreover, the concentration unit for the old standards is the demal, which is defined as the number of grams of KCl per kilogram of solution and is defined only for specific values, i.e., 71.1352: lD; and 0.745263: 0.01D. It is therefore desirable to redetermine the specific conductance of a primary standard with greater precision and accuracy using modern technology, to eliminate its dependence on the resistivity of mercury, and to replace the demal unit with molality.

To this end, we have designed an all glass conductance cell with a well defined geometry. The cell constant can be determined accurately to 0.02% based solely on geometric measurements. The cell is assembled from a single pair of electrode housings, fitted with interconnecting flanges, and a set of removeable intermediate tubes of accurately known cross-section and length. The distance between the electrodes can be adjusted by inserting individual tubes of this set.

The theory behind this approach is as follows. The specific conductance for a known concentration of electrolyte is a constant. The total effective cross-sectional area is a fixed value for a given cell and is composed of two parts in the NIST cell: A_o, the portion of the cell between the electrodes and the connecting flanges; and A_i, the diameter of the replaceable center tube. A_i must be accurately known and it is expedient if it is constant for all the center tubes. The distance l has two components: l_o, the portion of the fixed but unknown length between the electrodes and the connecting flanges; and l_i, the accurately known length of the i'th center tube. The resistance R_i is the measured quantity, and can be separated into two components: r_o, due to l_o and A_o; and r_i, due to the i'th center tube. Thus,

$$R_1 = (1/\kappa)(r_o + r_1) = (1/\kappa)(r_o + l_1/A_1)$$

and

$$R_2 = (1/\kappa)\,(r_o + r_2) = (1/\kappa)\,(r_o + l_2/A_2)$$

By performing the experiment with two center tubes of different lengths (but with $A_1 = A_2 = A$) and solving the simultaneous equations, κ can be determined:

$$\kappa = (l_1 - l_2)/(R_1 - R_2)A$$

Experimental results show that the values for 0.1D and 0.01D KCl at 25 °C agree with the Organisation Internationale de Metrologie Legale recommended values (which are based on κ for mercury) to within 0.02% which is the uncertainty for both sets of data.

4. Advancement of Robotics in Analytical Chemistry and Applications to Chemical Separations for SRM Certification

H. M. Kingston and F.C. Ruegg

Chemical measurement technology is undergoing extraordinary transformation and expansion from labor-intensive, single-parameter chemical measurements to automated, multi-parameter measurements. Applications include materials processing, food processing, waste management, and diagnostic technologies, affecting about two-thirds of the GNP. Rapid growth in applications has made chemical measurement technology the largest measurement technology used in the industrial and governmental sectors, accounting for more than half of the economic value of all measurements made each day with total annual expenditures estimated at $50 billion.

At the forefront of research in the areas of process and quality control techniques for chemical characterization is research in laboratory robotics and automation. Simple robotic systems already are being incorporated into industrial laboratories for high volume analyses. Development of expert systems control will greatly expand the capability of laboratory automation.

Analytical chemists and instrument manufacturers agree that sample preparation is a major impediment to fast, accurate instrumental analysis. As a sample preparation technique, separations procedures can be one of the most labor intensive. This system uses open-column ion exchange and chelation chromatography to isolate single elements or groups of elements at minor to trace (1% to 10 ng/g) concentration levels from the other components of a sample. These separations are necessary prior to quantitative determinations of the elements by instrumental techniques. The analyst enters parameters into a program that resides in a master computer which then converts these instructions into a robot control program for the desired separation. The robot is responsible for manipulation of samples and reagents through a series of preprogrammed operations activated by the master computer.

Entry of a new separation procedure into the master computer requires approximately 15 minutes while modifications of existing procedures require less than 5 minutes. Neither requires reprogramming of the robot.

This system applies new methods in the field of laboratory robotics. A major development is an interface control program that is "chemist friendly"; the chemist must only know the chemistry of the separation and not how to program robots. The system provides a hierarchical method for computer control of robotics and provides a functioning instrument capable of versatile chemical separations.

The robot and separation apparatus are located inside a small class 100 clean air chamber. This chamber provides the environment required for handling trace element samples to prevent contamination. Verification of each robot operation is accomplished by sensors, several of which were specifically designed for this system. A record of the operations performed on each sample during the separation is stored by the master computer and thus becomes a quality control document that is useful in quality assurance.

This system has been used to certify 4 elements in the new River Sediment, SRM 2704. Laser Enhanced Ionization was used to certify Mn, Ni and Pb while Graphite Furnace Atomic Absorption was used to certify Cd. Standard separations were also done by a separations chemist and compared with the robotically produced sample. No significant difference between the measurements was observed. This automated system is now being used to separate samples for certification in support of several instrumental analytical techniques. The concepts developed for this application are now being incorporated into a second system being developed for the EPA. The new system will be used to demonstrate the feasibility of applying new robot control technology to the decomposition of environmental samples using microwave preparation technology.

5. A Prototype Expert System for Developing Microwave Dissolution Procedures

F.A. Settle, Jr. and H.M. Kingston

Closed vessel microwave dissolution has proven to be an effective procedure for preparing a variety of sample types for analysis by several techniques. To function properly, a microwave procedure requires values for the sample mass, the identity and volume of the reagent(s) used for the dissolution as well as the temperature and time required for the digestion. These values depend upon four analytical descriptors that characterize the analysis: (1) the type of matrix represented by the sample, (2) the analyte(s), (3) the expected concentration level of the analyte(s), and (4) the technique to be used for the measurement.

A prototype expert system has been developed to assist the analyst in establishing procedures for microwave dissolution. The system first guides the analyst in selecting analytical descriptors for the sample and then uses these descriptors to recommend conditions for digestion of the sample. Once a procedure has proven successful, it can be stored for future reference. Thus, the system has the ability to "learn" new procedures.

The knowledge base of the expert system contains rules for : (1) matching the matrix of the sample with that of an SRM and (2) inducing the conditions for digesting the sample. A separate database component of the system contains detailed information on the elemental composition of the SRMs. This database was developed by the Inorganic Analytical Division to monitor the progress of SRM analyses.

The initial component of the system identifies the SRM most closely resembling the sample to be digested. If the analyst knows the name or number of the SRM corresponding to the sample, either can be entered directly. If, however, the analyst is uncertain as to the choice of SRMs, he can characterize the sample by responding to a series of multiple choice questions that allow the system to match the sample with an SRM.

Once the appropriate SRM has been determined, the analyst can review information in the database and select the set of analytical descriptors for the current analysis. The expert system now queries the analyst for the following additional information on the digestion: (1) the estimated moisture content of the sample; (2) the sample vessel (e.g., 120 mL Teflon PFA); (3) the number of samples per digestion; (4) the maximum power (watts) delivered to the sample cavity by the microwave unit. With this information and the analytical descriptors, the system recommends specific conditions for the dissolution.

While the prototype furnishes the conditions directly to the analyst, future versions will permit the system to interact with laboratory equipment including robots and programmable microwave units, to produce automated procedures. Work is also in progress to develop a system capable of storing successful microwave procedures developed in a number of laboratories and retrieving them for use in one of several laboratory environments: (1) totally manual; (2) manual sample preparation and automatic microwave dissolution; and (3) totally automated.

6. Development of Rapid Dissolution Procedures for the Determination of Volatile Elements such as As, Se, S, and Hg

M.S. Epstein

Dissolution procedures designed to prepare samples for the analysis of elements such as As, Se, S, and Hg by atomic spectrometric techniques are often time-consuming, since special measures must be employed to eliminate volatilization losses. The recent development of microwave digestion methods has made rapid sample preparation (1 hr) a reality, and the closed-system nature of this technique makes possible the determination of volatile elements using digestion parameters similar to those used for nonvolatile elements. We are presently investigating the application of microwave digestion as a sample preparation method for the determination of volatile and nonvolatile elements in sediment samples by ICP-MS, ICP-ES, and GFAAS. Results for SRM 2704 (Buffalo River Sediment) show significant promise.

Samples (0.5 g) are weighed into Teflon PFA vessels along with 9 g of HNO_3 and 4 g of HF. The vessels are sealed and exposed to 579 W of microwave energy for 15 minutes. Pressure and temperature are monitored throughout the digestion, with maximum values of 180 °C and 100 p.s.i., respectively. After completion of the digestion, the samples are cooled and transferred to plastic storage containers.

7. A Direct Solid Sample Introduction Method for the Determination of Trace Elements in Glass Using Zeeman AAS

Li-jian Yu and T. C. Rains

Solid sampling techniques for atomic absorption spectrometry with electrothermal atomization (ETAAS) have been considered for years to be an attractive approach for trace elemental determinations. The technique offers advantages such as a minimum of sample pretreatment which minimizes the chance of contamination or loss of analyte, speed of analyses, and low detection limits. However, the technique is not as precise and calibration is a major problem. With the advent of the L'vov platform, and Zeeman background correction, it is now possible to calibrate ETAAS for some types of materials using aqueous standard solutions. However, the technique is reported to suffer poor precision and many interferences. One possible explanation of the poor precision and accuracy is that the residence time of the analyte is changed by the additional convection gas flow induced by the expending matrix gases. If standards can be prepared to closely match sample matrix, such as a standard reference material (SRM), calibration of the ETAAS instrument is not a major problem. But SRMs matrices are limited and the analyst has resorted to the standard addition method. Standard addition has long been considered as an effective way to combat the multiplicative interferences in aqueous samples. The application of standard addition is based on the assumption that the analyte added is in the same chemical form as in the unknown sample. Usually this is not the case in solid samples.

In this work a new concept called in-situ digestion has been introduced. After the solid sample is introduced into the furnace a matrix modifier is added to dissolve the sample. As the sample is digested inside the absorption cell, the basis of the calibration for the solid sample can be set on the well-established solution ETAAS calibration technique. As a result, standard addition becomes effective for calibration of the solid sample. In our experiments with SRM 614 Trace Elements in Glass, we found that the analyte signal displayed a Gaussian distribution on the absorbance vs. T scale. In addition the background is greatly reduced, tube life is prolonged, and the precision and accuracy of the determination is improved.

The procedure involves weighing 0.2 to 1.5 mg of the solid material on a microbalance and then transfer it with the aid of a pipette tip, into the furnace on the L'vov platform. The matrix modifier which consists of a mixture of H_2SO_4 and HF is added. The temperature is raised and the glass matrix is volatized. Finally the analyte is atomized and absorption measured. The procedure is repeated except that after the volatization of the matrix, the tube is cooled and analyte spike added. Then the temperature is raised, the sample is charred and atomized, and the absorption is measured. The concentration is then calculated by the standard addition method.

At the beginning of our solid sampling experiment, SRM 614 was introduced directly onto the platform without any modifier. The analyte signal was erratic and after 100 determinations a round hole was found on the platform at the site where the solids were deposited. The graphite tube remained in good condition. This suggested that the matrix in the solid sample was attacking the graphite. A possible explanation is that the graphite platform is oxidized by the silicate forming silicon carbide. When the experiment was repeated using a matrix modifier, the effect was not observed.

Standardization using an aqueous standard calibration curve was also investigated. It was found that the analyte concentrations were consistently higher then the certified values for SRM 614. This would indicate that multiplicative interferences were being encountered and proper matrix matching should be used. Since Ca is present at a relatively high concentration in SRM 614, Ca was added to all standards to match the analyte matrix. As a result the analyte values for Co, Cu, Fe, and Ni were in good agreement with the standard addition methods and with the certified values. The overall precision of the method for Co, Cu, Fe, and Ni in the 0.5 to 1.5 mg range in SRM 614 was 10 to 12 percent.

Solid sampling is an attractive technique for its simplicity and straightforwardness. With in-situ digestion, matrix modification, and aqueous standardization, the technique is being investigated as a unique method for the determination of trace elements at the submicrogram level in highly refractory materials.

8. <u>The Development of Modern Approaches to Classical Analytical Chemistry</u>

T.W. Vetter, J.M. Smeller, and M.S. Epstein

Classical wet chemistry (titrimetry and gravimetry) is augmented by instrumentation-based trace analysis methods to decrease the analysis time required for classical analysis yet retain and often improve its high accuracy and precision. Direct-current plasma emission spectrometry (DCPES), inductively-coupled plasma emission spectrometry (ICPES) and flame atomic emission (FAES) or absorption spectrometry (FAAS) are used to characterize reagent blanks, to insure precipitate purity, and to monitor procedures (i.e., separations, extractions) for loss of analyte. Since the instrumental methods are used to determine only a small percentage of the analyte, their poorer precision and increased bias do not significantly degrade analytical results. Silica, sodium, calcium, iron, copper and nickel have been determined using this modern approach to classical analytical chemistry as described in the following examples.

(a) The classical gravimetric determination of silica in clays and sediment involves a double dehydration with HCl followed by filtration of a silica precipitate that is ignited and weighed. When the silica precipitate is filtered, a small amount of silica dissolves and is washed into the filtrate. The filtrate (containing 1% or less of the total silica) is usually recovered by precipitation with ammonia followed by additional tedious steps. Instead, silicon dissolved in the filtrate after the second filtration is determined by DCPES. In the analysis of 0.5 g of Buffalo River Sediment, SRM 2704 (SiO_2 = 62.22 ± 0.28 wt%), the silica dissolved in the filtrate ranged from 0.3 to 0.7 mg representing 0.1-0.2% of the total silica in the sample. Addition of this relatively small silica fraction to the total silica gives a more accurate and precise value.

(b) The classical determination of sodium involves several separations with a final weighing as sodium sulfate. For the determination in a river sediment matrix, a combination of $HClO_4$, HNO_3 and HF is used for dissolution. Iron, aluminum and co-precipitating elements are separated out by a double precipitation with ammonium hydroxide. Nearly all the sodium plus some other elements remain in solution. The small quantity of sodium trapped in the ammonia group precipitate is determined by FAES after dissolving the precipitate. The sodium remaining in solution after the ammonia group precipitation is separated from the remaining elements by elution on a cation exchange column (AG 50W-X8, 100-200 mesh) with 0.4 M HCl. The eluent collected prior to and after the elution of sodium is checked for trace amounts of sodium by FAES. After the eluted sodium solution is evaporated and H_2SO_4 is added, the solution is again evaporated to convert NaCl to Na_2SO_4. The Na_2SO_4 precipitate is ignited at 900 °C to constant weight. Possible contaminants in the Na_2SO_4 precipitate are determined by ICPES after fusing the precipitate with lithium metaborate and dissolving the melt in dilute HNO_3. Significant amounts of residual sodium have been found in the ammonia precipitate, but no significant contaminants have been detected in the Na_2SO_4 precipitate.

(c) Calcium is determined using an EDTA complexometric titration and a photometric endpoint. Calcium concentrations are determined in reagent sample blanks by DCPES.

(d) Iron is determined by titration with potassium dichromate. Ion-exchange or solvent extraction procedures used to separate matrix components are evaluated for recovery of separated iron by FAAS or DCPES. Contamination in reagents and sample blanks are also monitored.

(e) Copper in monel is determined by electrolysis of a sulfuric acid solution of the metal. Copper in solution is plated out onto a clean, pre-weighed platinum electrode. After plating is judged complete, the platinum electrode is reweighed to determine electroplated copper. Copper remaining behind in the solution, usually 0.1 to 0.2 percent of the total electroplated copper, is determined by ICPES. The copper plated on the electrode is dissolved with HNO_3 and contaminants are determined by ICPES.

(f) The gravimetric determination of nickel as nickel dimethylglyoxime is a widely accepted classical method. ICPES analysis of nickel in fractions separated from the nickel dimethylglyoxime and of contaminants in the nickel dimethylglyoxime precipitate is used to confirm results. In monel, copper must be separated from nickel prior to precipitation of the dimethylglyoxime. Copper is separated from nickel by electrolysis. The electroplated copper is analyzed for traces of nickel by ICPES. Nickel is separated from solution as a nickel dimethylglyoxime precipitate by the addition of dimethylglyoxime dissolved in ethanol. The nickel precipitate is collected on a clean, pre-weighed, fritted glass crucible. The crucible is dried and weighed to determine the weight of nickel as nickel dimethylglyoxime. The nickel precipitate is dissolved in HNO_3 and analyzed by ICP to determine possible contaminants. The solution separated by filtration from the nickel dimethylglyoxime is analyzed by ICPES to determine nickel.

9. The Determination of Tributyltin in Sediment Using Liquid Chromatography with Laser-Enhanced Ionization as a Tin-Selective Detector

G.C. Turk, K.S. Epler, and W.A. MacCrehan

A method has been developed for the determination of the antifouling agent tributyltin (TBT) in estuarine sediment based on liquid chromatographic separation of TBT from other tin compounds coupled with laser-enhanced ionization (LEI) as an atomic spectroscopic tin-selective detector. The cation exchange separation procedure provides a considerable advantage over other separation procedures developed for TBT in that it does not require chemical derivatization of the TBT cation. Other existing separation methods for TBT require the formation of TBT hydride or alkylation of TBT via the Grignard reaction. Concerns about the accuracy of methods requiring these derivatization reactions for the determination of TBT in sediments have been raised. The cation exchange method avoids this problem, but is a relatively low-efficiency separation, with plate counts of only 2800/m. Consequently, considerable chromatographic dispersion is encountered and a 100-fold dilution of the injected sample into the chromatographic mobile phase occurs. The high sensitivity of LEI allows detection of trace quantities of TBT despite this dilution factor. The limit of detection using the LC/LEI instrument is 3 ng/mL for tin as TBT using a 20-μL injection for an absolute detection limit of 60 pg.

For the determination of TBT in sediments, a n-butanol extraction procedure has been developed. An extraction efficiency of 97% with a relative standard deviation of 8% was achieved using this simple procedure, which can be performed in less than 30 minutes. A wavelength modulation technique was devised which can perform real-time spectral background correction. The relative complexity of the laser instrumentation required for LC/LEI is certainly a drawback, but the avoidance of chemical derivatization has a significant accuracy benefit, and the rapid extraction procedure is suitable for large scale survey studies.

10. The Determination of Ba-Y-Cu Oxide Stoichiometry in Superconducting Materials Using ICP Optical Emission Spectrometry

Laura J. Wood and Robert L. Watters, Jr.

Inductively coupled plasma (ICP) spectrometry was used to determine the stoichiometry of superconductor material. The chemical formula was known to be approximately $Y_1Ba_2Cu_3O_7$, and an ICP sequential spectrometer was used to scan the spectral analysis lines for Y, Ba, and Cu. Since oxygen is difficult to determine directly, the overall stoichiometry can be obtained by determining the other elements by chemical analysis and calculating the oxygen difference. However, the cumulative effect of errors in the individual determinations of Y, Ba, and Cu will result in a magnified uncertainty in the result for oxygen. Therefore, it is essential that random and systematic errors be minimized in the determinations of Y, Ba, and Cu. We used ICP spectrometry with simultaneous internal standardization to determine these elements with high precision. The typical relative error for ICP analysis at concentrations well above the detection limits is about 2%. This error is due to photomultiplier shot noise, plasma flicker noise and sample introduction flicker noise. In addition, long-term drift may cause errors of a few percent relative over hour-long periods if the instrument is not re-calibrated. When the chemical matrix of the sample is not complex and the spectral lines of interest exhibit signal-to-noise ratios of over ten, significant portions of the overall noise and drift characteristics are correlated from element to element. Under these circumstances a simultaneous measurement of the signal from a constant concentration of an internal standard element can be used to correct for correlated noise and drift.

Sequential ICP spectrometer systems measure spectral intensities of different elements at different times. Therefore, the measurement of an internal standard element spectral line intensity simultaneous with that of an analyte line is not always possible. The particular ICP spectrometer system used for these measurements has a separate filter photometer channel that continually monitors the 424.683-nm spectral line of scandium. This element is a suitable internal standard for many ICP applications. As each analyte spectral line is sequentially scanned, the scandium signal is also measured simultaneously. The background signal is subtracted from both the measured Sc intensity and the measured analyte intensity. The net analyte and Sc intensities are then divided for a final concentration value.

The superconductor material was supplied in powdered form. Several different samples were dissolved with an acid digestion procedure using 50% (V/V) HCl. The resulting solutions were then diluted to reduce the elemental concentrations to within the linear response range for ICP spectrometry. Scandium was added to each calibration standard and sample solution so that its final concentration was 50 μg/mL. Standard calibration curves for each element were established using a mixture of single-element stock standard solutions made from pure materials. Replicate integrations of each element scanned were used for each solution analyzed. When using internal standardization, the relative standard deviations of the replicate integrations are less than 0.4%. Without internal standardization, the relative standard deviations are approximately 2.0%. Yttrium, barium, and copper were determined in each sample analyzed. The Y and Cu values agreed with those reported by the Nuclear Methods Group for the same material, and the precision was approximately four times better than the nuclear technique.

The final calculation of the oxygen content also depends on an accurate assessment of the presence of trace impurities. The ICP system was also used to scan the spectral lines of 36 elements for a prototype sample of superconducting material. The following elements were detected: Al, B, Ca, Fe, Mg, and Si.

The Ba values were consistently low and varied by more than the expected uncertainty for analyses using internal standardization. This source of error is due to incomplete dissolution of Ba. Undissolved particles in the sample solutions were separated and analyzed by DC arc emission spectrometry. Ba was found in this residue, which was probably in an insoluble form resulting from the physical treatment associated with the superconducting material preparation. This point will be investigated further by analyzing a variety of superconducting materials resulting from different treatment procedures, and by employing high-pressure dissolution methods. Presently, the ICP method can be used to determine Y and Cu with accuracies and precisions of about 0.5% relative. The method requires about 2 hours to complete, which is rapid enough to be useful in evaluating prototype superconducting materials and processes.

11. The Technical Planning and Execution of a Certification Program for the Buffalo River Sediment SRM

M.S. Epstein

The program for the certification of SRM 2704, Buffalo River Sediment, was concluded in FY88. The program involved close cooperation between the technical coordinator designated by the Office of Standard Reference Materials and the technical champion designated by the Inorganic Analytical Research Division in the planning and execution of the SRM project. The implementation of well-defined quality control procedures for collection, processing, and analysis of the sediment, as well as improvements in analytical methodologies, have resulted in a reference material that is more completely characterized than previous NBS sediment reference materials. The sediment will be certified for at least 25 elements, with information values provided on more than 20 other elements.

Highlights of the certification program are as follows:

(a) Planning (April 1985) - Preliminary samples of sediment were evaluated for inorganic and organic constituent concentrations, homogeneity, and yield after freeze-drying and sieving. Material handling and preparation procedures were designed to be similar to those to be used for the bulk sample in order to identify potential difficulties. Homogeneity was assessed for 4 elements (C, Ca, Fe, Si), and semi-quantitative information obtained on 13 others. PAHs, PCBs, and pesticides were also identified in the preliminary samples. Sediment collected from the vicinity of the Ohio Street Bridge over the Buffalo River was chosen for the SRM.

(b) Collection (November 86) - The sediment was collected with the cooperation of the U.S. Army Corps of Engineers using a clamshell bucket suspended from the crane of a derrick boat. The sampling protocol was a compromise between the methods used in the collection of previous sediment reference materials (SRM 1645 and SRM 1646) in that small-scale sampling from a large collected sample was employed. A Teflon-coated shovel was used to transfer sediment from the clamshell bucket to Teflon-coated bags nested inside polyethylene-lined, 55-gallon steel drums.

(c) Processing and Preliminary Evaluation (FY87). The sediment was refrigerated and transported to a facility where it was mixed, freeze-dried, screened to pass a 100-mesh sieve, remixed, and placed into polyethylene-lined aluminum cans. The gross homogeneity was evaluated using 4 elements (Cr,Fe,Na,Si) and analysis of variance (ANOVA) to separate can-to-can, sample-to-sample, and instrument variance. Inhomogeneity was observed for Cr and Fe, and the sample was reblended in a cone blender. Subsequent evaluation of the reblended material indicated satisfactory homogeneity for these elements.

(d) Humidity/Drying Study (FY87). The behavior of SRM 2704 under varying environmental conditions was evaluated using a chamber equipped to do accelerated humidity and drying studies. The composition of SRM 2704 was found to be reproducible at a given %relative humidity and a sample dried to a reproducible composition when the recommended drying procedure (2 hours at 110 °C) was used. The nominal weight loss was 0.8%.

(e) Evaluation of Sediment Homogeneity (FY87-FY88). The homogeneity of bottled units of SRM 2704 was assessed using x-ray fluorescence (XRF) spectrometry for 12 elements (Al, Ca, Fe, K, Mn, P, Rb, Si, Sr, Ti, Zn, Zr) and graphite furnace atomic absorption spectrometry with slurry sampling for 4 elements (As, Fe, Mn, Pb). Homogeneity information for other elements was also obtained from certification analysis results by applying ANOVA to information provided by each analytical method.

(f) Analytical Measurements (FY87-FY88). The certification analyses were performed by 5 different laboratories using 19 different analytical methods. Each laboratory was provided with a set of instructions which detailed the number of samples to be analyzed, the drying procedure, the dissolution procedure, the control samples, and information which should be included with the reports of analysis. Analytical methods for a specific element were chosen to maintain maximum "independence" and both dissolution procedures and analysis methodology were included in the decision-making process.

(g) Statistical Evaluation of Data (FY88). The certified values were calculated as the weighted mean of results from two or more independent analytical techniques. The uncertainty in each certified value was calculated as the sum, in quadrature, of estimates for material inhomogeneity, and random and systematic errors among the methods used for certification.

As a result of the NIST certification program for SRM 2704, not only was the sediment characterized for more elements than previous NIST sediment SRMs, but also the confidence limits for certified values were decreased by almost two fold.

12. Measurement of Chromium in Human Blood and Blood Fractions at Natural (sub-ppb) Levels

R.R. Greenberg and R.L. Zeisler

Chromium was recognized as one of the elements essential for humans more than twenty-five years ago. However, at elevated concentrations, some forms of Cr are toxic and possibly even carcinogenic. In recent years, several analytical techniques have demonstrated the capability to accurately determine chromium at the naturally-occurring, ultratrace-levels normally found in uncontaminated samples of human serum. A variety of problems, however, have limited the determination of Cr to this single fraction of human blood. In view of the importance of this element, more detailed investigations of its occurrence and role at natural levels are needed, requiring even more sensitive analytical methods.

A reliable radiochemical procedure for Cr has been developed based upon neutron activation followed by a radiochemical separation. The separation procedure involves the liquid/liquid extraction of Cr(VI) into a 5% solution of tribenzylamine/chloroform, back-extraction into an aqueous solution (2 mol/L) of sodium hydroxide and precipitation as barium chromate. Radiochemical neutron activation analysis (RNAA) is one of the best analytical techniques currently available for trace and ultratrace level determination of Cr in biological materials. It possesses the sensitivity required to determine sub-nanogram amounts of Cr, and the nearly blank-free nature of the technique allows chemical dissolution and separation of Cr from the sample matrix (after irradiation) without regard to reagent blank. In addition, NAA is free from chemical interferences, and most types of matrix effects which can interfere with other, non-nuclear, analytical techniques. However, the nuclear interference from the fast neutron reaction Fe-54 (n, alpha)Cr-51, can be significant. This interference can be minimized, however, by using a highly thermalized facility such as the RT-4 facility of the NIST Research Reactor. In this facility, the measured Fe interference is 0.087 μg of Cr per gram of Fe, or approximately two orders of magnitude lower than that experienced in a typical light water reactor. The RT-4 interference is equivalent to a Cr blank of 0.039 ng of Cr per gram of whole blood for men, and 0.035 ng/g for women.

Chromium concentrations have been determined in whole-blood samples from nine individuals. The Cr concentrations for eight of these people were between 0.04 and 0.3 ng/g on a fresh weight basis. The ninth individual had a considerably higher level of Cr, and this is discussed below. Serum samples have been analyzed for seven of these individuals, and packed cells for two. Duplicate samples from a single collection have been run for the whole blood from one person and for the serum from a second. Both duplicate values are consistent with the observed counting statistics. In addition, blood from these two individuals has been sampled on two occasions more than one year apart. No differences in the Cr concentrations, greater than the analytical uncertainties, can be seen for subject B2. A small, but real, increase in both the whole blood and serum Cr levels from B1 was observed. It should be noted that between the 1986 and 1987 sample collections, individual B1 was taking a daily dietary supplement containing 200 μg of Cr in the form of an amino-acid chelate, while no supplement was taken prior to the 1986 collection. This factor of five increase in Cr intake, compared to the average American dietary intake of approximately 40 μg/day, resulted in a Cr increase of approximately 50%, by weight, for whole blood in men. There appears to be no change in the Cr concentration in the packed cells of this individual. The large increase in dietary Cr had only a relatively small effect, elevating the serum level for B1 from the second lowest concentration observed in this study, to the median value. Thus, at least for this individual, Cr levels in the blood may be under some type of bioregulatory mechanism.

An interesting observation can be made concerning individual T2. This person had concentrations of Cr in both whole blood and serum which were elevated by factors of 5-20 compared to the other individuals studied. Subsequent questioning revealed that this person has been diagnosed as a borderline diabetic, and has a family history of diabetes (mother). In view of the possible link between Cr and glucose metabolism, further studies of the Cr concentrations in whole blood and blood fractions from diabetics may be indicated. However, in view of the difficulty in making accurate Cr determinations, at the naturally occurring levels in these materials, carefully validated analytical methods and rigorous quality assurance procedures should be used for these studies.

13. Measurement of Long-Term Stability of Human Livers

R.L. Zeisler, R.R. Greenberg, S.F. Stone, and T.M. Sullivan

At present, only limited data are available on the long-term storage of biological materials. For the storage of biological tissues and fluids, rapid freeze drying immediately after sampling has been recommended. However, this technique suffers from the disadvantage that some volatile components may be lost. In freeze-dried materials, trace element concentrations are stable over an extended time period even if stored at room temperature, as has been shown in various NIST Standard Reference Materials. Another approach is the immediate freezing of the sample or sub-sample to the lowest conveniently attainable temperature. This approach serves two purposes: 1) it reduces or stops chemical and biological processes which could result in sample changes, and 2) it reduces the mobility of constituents in the sample and/or container material, thereby lessening the possibility of contamination and/or losses due to absorption/adsorption or volatility. A subsampling, storage, and analysis program was designed to lead to a complete evaluation of the storage processes with respect to the long term preservation of the originally present trace constituents over a several years storage time. To solve the question of the most appropriate temperature for sample storage, aliquots of the specimens were stored under four different conditions: freeze dried at room temperature, frozen at -25 °C, at -80 °C, and in liquid nitrogen vapor (LN_2) at -120 °C to -150 °C. The concentrations of trace constituents found after storage under those conditions were compared to the data found in the analysis of each specimen, The statistical assessment of the probability for discovery of changes included consideration of sample inhomogeneity, variations among aliquots, analytical error, and number of specimens analyzed. A 98% probability existed to detect a 6% change in the concentrations if 30 livers specimens were analyzed, and the errors due to inhomogeneity and analysis would be limited to 5% each.

The human liver specimens were collected in the pilot National Environmental Specimen Bank (NESB). They were cryogenically homogenized, aliquoted into Teflon jars and distributed to the different storage facilities and the baseline analysis in 1980. For the initial investigation, aliquots from 24 specimens were removed from the -25 °C and LN_2 storage in 1987 and analyzed by neutron activation analysis. The results were compared to the baseline data.

This study covered elements that form stable ionic and/or molecular species in tissues as well as elements that form or are converted to volatile species in metabolic processes. No difference was observed between those categories. No deviation could be determined that exceeded the calculated statistical boundaries, although physical segregation into ice and lumps of material instead of powder was observed in the -25 °C storage. Although storage at -25 °C is easier to achieve, the observed sample degradation points towards sample storage at -80 °C or LN_2 as the storage condition of choice. These results confirm that Specimen Banking is a feasible tool in environmental monitoring. In addition, the established total element stability of fresh frozen biological materials may very well be valid also for elemental species. Consequently, this type of storage should be used as reference in speciation studies.

14. Quantitative Determination of Proteins Using Polyacrylamide Gel Electrophoresis and Neutron Activation

S.F. Stone, R.L. Zeisler, and G.E. Gordon

The accurate determination of trace element content and function in macromolecules requires an analytical scheme that combines a highly sophisticated biochemical separation with a highly sensitive and accurate analytical technique. Polyacrylamide gel electrophoresis (PAGE) is a rapidly developing and widely used biochemical separation technique. It has excellent resolution for proteins and other charged macromolecules. Much of the work done with PAGE has involved using radionuclides as "tracers" for the detection of proteins following separation. This work utilized both in vivo labeling prior to electrophoresis and in vitro labeling after separation, where an exchange of non-radioactive for radioactive trace elements has taken place. These studies have used radiotracers as a qualitative detection technique in lieu of staining methods, rather than for the quantitative determination of the trace elements associated with the proteins. To overcome the necessity of radioactive labeling, we have investigated the possibility of identification and analysis of these separated proteins with neutron activation analysis (NAA).

A method has been developed that combines the powerful separation capacity of PAGE with the sensitivity of NAA. This method involves the neutron irradiation of the whole gel containing the separated proteins, and detection and quantitation of the produced radionuclides by autoradiography and gamma spectrometry. The principle of PAGE/NAA applied to some macromolecules has already been shown in previous work; i.e., the qualitative detection of phosvitin and carbonic anhydrase. Similarly, phosphorous in adenosine triphosphate (ATP) separated by thin layer chromatography has been quantified following irradiation. In our work, phosphoproteins were selected as a model to study this method. Quantitative measurements of phosphorus in phosphoproteins separated by both sodium dodecyl sulfate (SDS)-PAGE and non-denaturing PAGE have been accomplished. Linear concentration relationships are being demonstrated with absorbance measurements of developed autoradiographs using laser densitometry. The method is also being applied to determine the concentration of caseins in a "natural matrix" sample, Standard Reference Material (SRM) 1549, milk powder.

This protein quantitation method has been shown to be feasible for phosphoproteins. The method provides an important research tool for protein investigations, such as in human samples, where labeling is difficult, and, in most cases, simply cannot be done. PAGE/NAA will also be useful in speciation studies, where the excellent resolution of PAGE coupled with the sensitivity of NAA will be well suited. The work is currently expanding to include other proteins, e.g., selenoproteins, and appears to be applicable to protein samples within normal concentration ranges.

15. Determination of As, Cd, Cr and Mo in the NIST Bovine Serum Standard Reference Material at the PPB Level

R.R. Greenberg, R.L. Zeisler, and T.M. Sullivan

As bioanalytical methods for trace element determinations have become more sensitive, biological and medical trace element research has included studies of many of the "difficult" elements such as Al, As, Cd, Cr, Mo, Mn, Sb and V. These elements are currently of interest, for example, in human blood-serum where they typically occur at the low ng/g level or below. The accurate determination of trace elements at these levels usually requires certified reference materials for method evaluation, and for quality assurance purposes. This need for low-level reference materials for accurate analyses of human-blood serum and related materials has been well-documented. To help meet this need the National Institute of Standards and Technology and the Department of Agriculture have cooperated in the production and certification of a frozen Bovine Serum Standard Reference Material (SRM) with uncontaminated, or nearly uncontaminated, levels of a wide variety of trace elements.

The certification of trace elements in this Bovine Serum (SRM 1958) was particularly difficult due to the very low levels of many of the elements of interest. A variety of analytical techniques has been used at NIST for the Bovine Serum certification. For several of these techniques, it has been necessary to extend their applicability beyond previously demonstrated measurement competence. One of these analytical techniques, neutron activation analysis (NAA), was used to determine the concentrations of most of the elements desired for certification. In addition to the instrumental measurements, a number of difficult, low-level elements have been determined with appropriate pre- or post-irradiation chemical separations.

Two radiochemical separations have been used to reduce interferences from matrix activities such as from Na, Br and P, or in some cases to totally isolate the element of interest from essentially all other radionuclides. Post-irradiation separations are particularly useful for low-level determinations since no reagent blank has to be considered. Arsenic, along with Mo, has been determined using the inorganic ion exchanger HMD, and Cd along with Cu, have been determined in the eluent from the same samples using sequential extractions into solutions of bismuth and zinc diethyldithiocarbamate in chloroform. This previously-developed procedure was modified to include a predigestion setup using a microwave oven. Dissolution was then completed with nitric and perchloric acids in a conventional manner (on a hot plate). The predigestion step allowed complete sample decomposition in two to three hours instead of the two days previously required to insure complete destruction of the organic sample matrix. This reduction in sample decay time improved the signal (number of counts) for As and Cd by factors of four and two respectively, and resulted in a comparable improvement in the detection limits. Arsenic and Cd were observed in the Bovine Serum at 0.15 and 0.093 ng/g respectively, while Mo was present at 11 ng/g.

Chromium has also been determined in the Bovine Serum SRM following a post-irradiation extraction of Cr(VI) into a solution of tribenzylamine in chloroform. This newly developed procedure has been applied to human blood and blood fractions, and is described elsewhere in this report. The Cr concentration in the Bovine Serum was 0.18 ng/g.

In addition to the elements determined after a radiochemical separation, three other biologically-important elements, Al, Mn and V, which are present at ng/g and sub-ng/g levels, have been determined previously in this material utilizing NAA combined with a pre-irradiation, chemical separation. These NAA results, when combined with the results from other analytical techniques, will allow the certification of many of these difficult elements in a natural matrix material. The new Bovine Serum SRM should be of great value for method development, and for quality assurance purposes when researchers analyze blood-serum or related materials.

16. Standard Reference Materials

W. F. Koch

This year marks a milestone for the Division's implementation of the "Technical Champion", with the completion of the first two major Standard Reference Materials (SRM) under this program. The Technical Champion (TC) is selected from the senior research staff to interact with the designated Project Managers in the Office of Standard Reference Materials (OSRM) for a specific SRM or class of SRMs. The TC is responsible for all technical aspects of an SRM from the selection and collection of a material, through the experimental design for analysis, to the assignment of certified values. The TC coordinates his efforts with Division management, OSRM, the analysts, and the statistician. The two SRMs formally issued under this approach are SRM 2704, Buffalo River Sediment, and SRM 1598, Bovine Serum. Both are the finest quality reference materials available for environmental and clinical applications, respectively, and stand as testimony to the effectiveness of the TC approach. Several other projects utilizing TC's are underway, most notably replacement SRMs for Oyster Tissue and Citrus/Orchard Leaves, and a new Total Diet SRM.

As the demand for high quality reference materials increases, especially those certified for ultra-trace levels of elements, the specifications for material suitability and homogeneity become more stringent. Considerable emphasis is now placed on preliminary research on candidate materials to identify potential problem areas that could be encountered during the actual certification process. This research includes careful material selection and processing, sample dissolution studies, homogeneity determinations, and weighing form (drying) studies. New methods of analysis are developed and existing methods are improved to keep ahead of the demands. Whereas this deliberate approach guided by a TC must begin two or three years before the actual certification process can begin, it is felt that in the long run it will provide better, more cost-effective, and more timely reference materials.

Funding for the reference materials program within the Division comes from various sources. An estimated 50% of the Division's base funding is directed toward reference materials. OSRM provides research and materials development support, and analytical services funding for actual SRM certification. This last item accounts for approximately 18% of the total budget of the Division. Of this amount, 80% is for renewal SRMs. Other government agencies, as well as private sector institutions, are often the prime sources of funding for the development of new reference materials.

Listed below are some of the areas of research specifically funded by OSRM during FY88. These projects often involve cooperative work by the scientific staff from all four groups in the Division.

STRS Projects Supported by OSRM in FY88

Task	Description
Mercury in Soils	Research to develop methods and procedures for determining mercury in soils and sediments using ICP. Work is in progress studying the application of combustion/absorption method of mercury introduction into the ICP.
Marine Sediments	Research to develop procedures for characterizing marine sediment in terms of physico-chemical parameters and trace constituent profile. Selected marine sediments have been collected and are being evaluated. This work should lead to an SRM.
Classical Analysis	Research to refine and adapt classical gravimetric and titrimetric procedures for use in the certification of elements such as Ca, Mg, Al, Na, Si, Fe, Ti, and K in select SRMs. Primary objective is to improve precision and accuracy of the certified values of major constituents.
Transient Standards	Research to develop methods and procedures for producing standards for metal speciation. The approach is to perfect a method of sealing small amounts of methyl mercury, ethyl mercury and mercuric chloride in glass and of providing the means to achieve dilution to working concentrations in the ppb range by the user.
Mercury Speciation	Research to develop procedures for the determination of mercury species in selected biological and environmental SRMs, using LC-ICP/MS. The LC is used to resolve the species; the ICP/MS provides high sensitivity for quantitation at the ppb level.
High Ionic Strength pH	Research leading to the certification of pH buffers in moderate to high ionic strength. This year a new pH buffer SRM, intended for use in physiological measurements, has been certified.
Phosphate/Nitrate Stability	Research to establish the stability of phosphate and nitrate anion standard solutions at the 1000 mg/L level. Results indicate that these solutions are stable to within 1% for at least one year. SRMs will be considered for next year.

This year analyses were carried out on more than 100 different SRMs covering a wide variety of matrices including metals, fossil fuels, foods, glasses, and environmental materials. Also included in this number are over 50 spectrometric solution standards. In most cases, each certification involved several or all of the Groups in the Division and required 20-30 individual analyses on each SRM. Examples of the SRMs worked on during the past year are listed below.

Standard Reference Materials Analyzed During FY88

SRM Number	Title
112b	Silicon Carbide
136e	Potassium Dichromate
679	Brick Clay
919a	NaCl
930d	Glass Filters
935	Potassium Dichromate
935a	Potassium Dichromate
955	Lead in Blood
1074b	Calcium 2-ethylhexanoate
1515	Apple Leaves
1547	Peach Leaves
1548	Total Diet
1566a	Oyster Tissue
1598	Bovine Serum
1616-1617	Sulfur in Kerosine
1623b	Residual Fuel Oil
1624b	Distilltae Fuel Oil
1634b	Trace Elements in Fuel Oil
1764	Low Alloy Steel
1766	Low Alloy Steel
1834	Simulated Fused Ore
2034	Holmium Oxide Wavelength Standard
2137	Boron Implant in Silicon
2165	Low Alloy Steel
2181	HEPES pH Buffer
2182	HEPESate pH Buffer
2416-2418	Lead
2677a	Arsenic and Beryllium on Filters
2692	Sulfur in Coal
2694-I	Simulated Rainwater
2694-II	Simulated Rainwater
2695-High	Fluoride in Vegetation
2695-Low	Fluoride in Vegetation
2704	Buffalo River Sediment
2712 through 2715	Reference Fuel
3101 through 3169	Spectrometric Solutions
3171	Multi-Element Spectrometric Solution A
3172	Multi-Element Spectrometric Solution B
3181	Anion Solution SO_4
3182	Anion Solution Cl
3183	Anion Solution F
3191	Conductance Standard 100 µS
3192	Conductance Standard 500 µS
3193	Conductance Standard 1000 µS
3194	Conductance Standard 10000 µS
3195	Conductance Standard 100000 µS

Among the SRMs being considered for next year are replacements for SRM 909, Human Serum, SRM 1043b Trace Elements in Water, and new materials for carbonaceous marine sediment, electrolytes in human serum, and trace elements in bone.

17. Analysis of U.S. Dietary Collections in Conjunction with the IAEA-NIST-FDA-USDA International Nutrition Project

V. Iyengar

An international human nutrition project sponsored by the International Atomic Energy Agency (IAEA), and supported by the U.S. National Institute of Standards and Technology (NIST), the U.S. Food and Drug Administration (FDA), and the U.S. Department of Agriculture (USDA) is in progress. This study is designed to assess the daily intake of certain dietary components by selected target populations in several countries. The countries involved are Australia, Brazil, China, Iran, Italy, Spain, Sudan, Sweden, Thailand, Turkey and the U.S.A. Mixed total diets from these countries are being analyzed for caloric energy, phytate and fiber content, and minor and trace elements. Analyses for these constituents are being carried out in selected reference laboratories identified by the IAEA. The NIST is one such reference center asked to determine a select group of inorganic elements.

The U.S. is involved both as a collection center and as a reference laboratory. A part of the study was concerned with evaluating analytical approaches. Mainly neutron activation analysis was used in both the instrumental and radiochemical modes. Guidelines were developed for the preparation of mixed diet reference standards for quality control, and one material (Mixed Diet SRM 1548) is currently being characterized for certification. Simultaneously, collection of U.S. mixed diets based on the FDA Total Diet Study scheme was initiated. Until now, six such collections have been completed from the following regions: Southeast (GA, TX, WV), North Central (IA, KS, OH), Northeast (NY, PA, RI), South (AL, LA, TX), West (AZ, CA, OR), and Central (IL, IN, WI). One portion of mixed diet, from each of the six collections has been stored in the Specimen Bank. Studies are also in progress to assess long-term stability of organic nutrients in mixed diets, under different storage conditions.

Five of these diets have already been analyzed for vitamins, fiber, phytate, and several minor and trace elements. The results obtained for several elements show remarkable agreement with the daily intake data calculated from the individual food analysis results of the FDA-TDS study, confirming the validity of the mixed diet approach for monitoring the daily intake of minor and trace elements. The results did not indicate any significant inter-regional variations in the overall daily intake. This is attributable to the fact that these U.S. collections represent national diets due to standardized collection procedures of the TDS scheme. In the present study, analytical results obtained for over 30 elements for the mixed diet samples provide a basis for establishing baseline values for the daily intake of a number of elements that are not covered by the FDA-TDS scheme.

18. Particle-Particle Coincidence Neutron Depth Profiling (NDP)

W.-K. Chu, N.R. Parikh, E.C. Frey, M.L. Swanson, and Z.H. Zhang, University of North Carolina, T.Z. Hossian, Eastman Kodak, and R.G. Downing and R.F. Fleming, National Bureau of Standards

During the previous year, NDP was modified to use a particle-particle coincidence technique which has the advantages of reducing the background, providing greater sensitivity, and increasing the depth of analysis. NDP takes advantage of the fact that a few nuclides of significant technological importance decay upon the absorption of a low-energy neutron by emitting a light charged particle, the recoil particle, and in some cases a photon. The two recoiling fragments are emitted isotropically from the reaction but along diametrically opposing paths. Initially, each reaction product has a known, well-defined energy. In conventional NDP, a single detector is used to determine the residual energy of a small fraction of the particles that escape one surface of the sample in order to establish the concentration versus depth profile of the element. However, given a sufficiently thin sample, both particles will escape from the sample and two appropriately positioned detectors will detect, in coincidence, both of the particles from a single reaction. Thus, for coincidence NDP the sample of interest, illuminated with neutrons, is placed between two facing detectors that are separated by a few centimeters. A decay event is recorded only when the products are detected simultaneously in two detectors. The energy of the first particle is determined and plotted against the energy of the second particle. The third axis indicates the number of events occurring with that particular energy combination. Imposing these criteria, a three-dimensional histogram is generated.

The background correction is much reduced by this approach because random coincident events are infrequent at the count rates typically encountered with NDP. As a result, the lower energy portion of the spectrum can be used, thereby increasing the depth of analysis without extensive background corrections. Because the background is reduced, detectors can be moved closer to the sample, thus increasing the counting efficiency. On the other hand, reducing the detector to sample distance increases the acceptance angle of the detectors which degrades the overall depth resolution of the profile. This is because the range of particle path lengths accepted in the detector is increased for a given depth of reaction. By using the mathematical method of Jacobians to convert the data from energy space to distance and angular space, the energy broadening from the measured spectrum can be effectively removed. Also, the model for the detector response function suggested by Lee, et. al., is being investigated in order to improve the overall depth resolution. By adapting these methods for use in coincidence NDP, the detectors are being used in a closer configuration than previously possible.

An additional logical constraint may be imposed upon the data since both the stopping power of the sample and the total energy of the reaction is known. The residual energies measured in the two detectors must be consistent with a single value for the depth of the reaction, within the energy resolution of the measurement. Those events which are inconsistent with this test are rejected. This provides additional confidence and greater accuracy in defining the depth profile.

Particle-particle coincidence NDP will have important applications in the study of interfacial distributions of lithium and boron found in many of today's advanced semiconductor and optical signal processing materials. Specialized equipment has been obtained and computer programs are being developed to perform the decision logic on data collected by this technique. The technology developed by this approach will be especially important for lower flux research reactors, allowing effective use of NDP at these facilities.

19. Measurement of Superconductor Stoichiometry by Prompt and Delayed Neutron Activation

Richard M. Lindstrom

Materials analysis provides essential information for understanding the physics of high-temperature superconductors and developing the production processes for their industrial application. Knowledge of the stoichiometry of sample materials, particularly the oxygen content, is important. Although oxygen is difficult to measure by activation with reactor neutrons, it may be determined by difference if the concentration of other elements are known. Prompt and delayed neutron activation analysis has been applied to the measurement of the metals in $YBa_2Cu_3O_7$ superconductors, starting materials, and intermediate products.

The low production cross section and low gamma energies of Y-90m make the determination of yttrium imprecise in the presence of high Cu-64 activity. The Poisson precision for Y determinations is 2% in practice, which is helpful but inadequate for the needs of researchers.

The physical parameters for neutron-capture prompt gamma-ray activation analysis (PGAA) are more attractive than delayed counting for stoichiometry measurements. The PGAA spectra of Y, Ba, and Cu show three, four, and six analytically useful gamma-ray lines respectively. Moreover, the relative intensities from the three elements are comparable for the composition range of interest. In the Maryland-NIST PGAA facility, a 100-mg sample gives a Poisson precision for yttrium (the weakest element) better than 1% in an 8-hour irradiation, which is adequate for determining stoichiometry of laboratory samples. Since the concentrations and mole ratios Y/Cu and Ba/Cu can be calculated immediately after the irradiation ends, the results can be available within a day.

Compositional measurements of substituted superconductors have been made in collaboration with the neutron scattering group. In these materials nominally 3-8% of the Cu had been substituted by Al, Fe, Ni, Zn, or Ga. Classical delayed activation analysis was used to measure the substituent and copper. The M/Cu ratios were not always as expected.

20. Development of an Intentional Isotopic Tracer for the Study of Particulate Emissions into the Atmosphere

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It is commonly believed that emissions from industrial and power plant stacks can travel great distances and cause deleterious environmental effects at sites far removed from their sources. One of the most important problems in atmospheric science is to determine the relative contributions of regional and distant sources on air and deposition quality. Chemical elements and compounds believed to be indigenous to particular types of sources have been used as tracers of opportunity in efforts to distinguish between regional versus long range transport of emissions from oil-fired and coal-fired sources. It is claimed that by using a multielement tracer system, the signatures of North America and Europe can be resolved several thousand kilometers downwind. However, tracers of opportunity are not unique to single sources, rather they can be common to a large category of sources, and thus do not yield definitive source-receptor relationships. The true relationship between emissions from a particular source and a receptor site have never been determined by direct experimental measurement. The ability to trace fly-ash emissions from utility coal-fired power plants and to measure particulate deposition to natural surfaces is important to the electric utility industry.

Many of the difficulties discussed above can be overcome by the use of an intentional tracer to tag primary emissions from utility sources. If successful, this approach would readily permit direct determination of source impacts on air quality and deposition independent of dispersion models, receptor models, or micrometeorological methods and thus permit their independent evaluation. While intentional tracers have been used successfully in dispersion and deposition studies, they have not been widely used to tag primary particulate emissions from large high-temperature combustion sources such as coal-fired power plants. The principal reasons for this lack of application include toxicity, chemical or radiologic instability, inadequate sensitivity, and high cost of the tracer material. The application of enriched rare-earth (RE) isotopes as intentional tracer materials may avoid all of the above difficulties.

The use of enriched RE isotopes as intentional tracers is a new technique and promises to be a powerful approach to aerosol particulate tracing well suited for use in power plant studies. The concept is very simple and consists of four parts: injection of the tracer, tagging of the particulate emissions, collection of the samples, and chemical and mass spectrometric analysis of the sample. In principle, the use of enriched isotopes of a single rare earth-element such as Nd or Sm, permits the simultaneous tagging of 5 different power plants. The measurement by thermal ionization mass spectrometry (TIMS) of the isotopic composition of airborne particles and natural surfaces at some distance from the plants permits the contributions of the individual plants to be apportioned at a receptor site. Since there are no natural or industrial sources of enriched RE isotopes, the detection of an enrichment is definitive evidence that emissions from a tagged plant have been measured. Use of additional RE isotopes would permit definitive and simultaneous resolution of multiple source impacts on individual receptor sites.

An enriched isotope of the rare earth element (REE) neodymium (Nd) has been investigated to demonstrate feasibility of the technique. Since the relative isotopic abundances of the REE are constant in nature, and can be measured with high precision (0.002%, relative) by mass spectrometry, a small induced enrichment can be readily resolved. Measurement of this enrichment would constitute definitive evidence that the tagged source had been detected. The uniqueness and power of the technique is that each tagged source has a unique isotopic signature which permits the relative and perhaps absolute contributions of multiple sources at a single location to be de-coupled by mass spectrometric analysis of the sample. Chemical and mass spectrometric procedures were developed to dissolve various types of samples, separate Nd with high purity and yields by cation exchange chromatography, and measurement of the isotopic composition and concentration of the Nd by thermal ionization mass spectrometry. In field tests in which the ^{148}Nd tracer was injected into the stack of a coal-fired power plant, we were able to detect large induced isotopic effects at mass 148 by mass spectrometric analysis of size fractionated samples collected down stream from the injection port.

Phase I of the project has been successfully completed. Isotopically enriched 148Nd was injected into the stack of a coal-fired power plant in the form of highly mobile and highly charged ultrafine particles. Thermal ionization mass spectrometry analyses of size-segregated stack-emitted fly-ash particles show that nearly all of the tracer material becomes attached to fly ash particles and that all sizes are tagged. Our original calculations suggested that ^{148}Nd could be detected with a 500:1 signal-to-noise ratio in ambient aerosols 100-km distant from a 425 MW(e) coal-fired power plant tagged with an injection rate of only 140 mg ^{148}Nd/hr. Results of the Phase I study suggest, however, that effective tagging can be achieved with even less tracer material because of the high tagging efficiency achieved for all particle sizes. Results of a preliminary experiment conducted in a soybean field further suggest that measurement of deposited plume particles can be made directly on vegetative surfaces in the vicinity of the tagged plant. The high precision and accuracy of TIMS, combined with improved air-flow monitoring techniques now available, should permit more accurate measurement of deposition by the gradient technique.

Based on the results of Phase I the enriched rare-earth isotopic tracer technique is believed to have potential as a research tool for application in studies of plume dispersion, source apportionment, and particle deposition. The Phase I reseach was supported by a grant from the Electric Power Research Institute, Palo Alto, CA.

21. Production and Analysis of Ultrapure Acid from a Large Teflon Still

J.R. Moody, E.S. Beary, D.S. Bushee, and P.J. Paulsen

The sub-boiling method of distillation from quartz stills has been employed at NIST. Aside from limitations of distillation rate (~0.5 - 2L/day), the only dissatisfaction with these stills has been the inability to significantly improve reagent purity. As instrumental techniques have improved, the demand for lower analytical blanks has increased.

High throughput was seen as a possible method of improving distillate quality while retaining the advantages of sub-boiling distillation. The services of the Fluoroware Corp. were engaged in order to fabricate a large still wholly from Teflon PFA, using designs provided by NIST.

In one year, three versions of these stills have been fabricated and evaluated at NIST. Distillation rates of up to 45 L/day have been achieved for the more volatile reagents such as HCl (10 N), H_2O, HF, and HNO_3. The ICP/IMS has been employed to measure the resultant reagent purity.

Recently, we have been able to expand upon our published work by increasing the number of elements, measured (from 35 to >60), improving our detection limits to <0.1 pg/g in some cases. We have now been able to demonstrate a 10-fold improvement in HF purity as a result of the new still.

Other acids such as acetic acid are also amenable to distillation and will be evaluated in the near future. Both the quantity and quality of reagent have been improved by the new still. The ICP/MS technique has been developed to the point where significant differences in purity at the pg/g level can be measured.

22. The Development of Multielement Procedures for Analysis of Diverse Materials by ICP-MS

P.J. Paulsen and E.S. Beary

The inductively coupled plasma mass spectrometry (ICP-MS) is a highly sensitive technique that has broadly applicability across the periodic table. We have continued to investigate its capability for accurate and precise measurement using isotope dilution. We have also developed methods for multielement analysis using internal and external standards. As the instrumentation has evolved, its capabilities for accurate and sensitive measurement have continually improved.

Isotope dilution analysis with ICP-MS has been applied to the determination of Cu, Sr, Ag, Cd, and Pb in Oyster Tissue SRM 1566a. Although the chemistry for the SRM was handled as a true multielement procedure, the elements were initially analyzed one at a time on the ICP-MS. This approach utilized a rapid repetitive scan of a mass range limited to just the element of interest. It provides both high sensitivity and the lowest error due to changes in instrument sensitivity and mass bias with time. The results of the spike calibrations yielded precisions of ±0.3% and agreed with thermal mass spectrometry calibrations of the same spikes to 0.3% accuracy. The samples themselves showed one percent or more variation due to sample homogeneity problems.

The same sample solutions were then reanalyzed for Sr, Ag, Cd, and Pb simultaneously, using the peak hop mode. Since only two masses per element need to be measured for isotope dilution, only a moderate loss of sensitivity was encountered compared to the single element scan mode. We had not used the peak hop mode previously since accurate data requires a much more stringent control of the mass scale stability than with the scan mode. Recent instrument improvements have made the peak hop mode a more practical alternative. Comparison of the peak hop isotope dilution results with the scan mode data showed good agreement. However, we did observe minor but real differences in concentrations between the two techniques of data collection. The differences were traced to errors from the higher count rates for the peak hop mode (instrument sensitivity was improved between the two experiments). Further experiments indicated that these errors are caused by gain losses in the ion multiplier (between $2x10^5$ to $1x10^6$ cps) which drop pulses below the pulse height discrimination set point. We are currently trying to determine if this is caused by the known drop in multiplier gain in this count range, or if it is an early indication of multiplier failure from catastrophic gain losses which occurs only at the very high count rates.

Multielement analysis using external standards alone, and in combination with internal standards, was evaluated in the analysis of air filter samples. An external standard containing ~30 elements at 30 ppb and internal standards of Sc (45 amu) and Tm (169 amu) were run often throughout these analysis. Data from these standards was used to evaluate the possibility of compensating for shifts of instrument sensitivity with time.

The external standard program assumes a linear shift in sensitivity with time on an element by element basis. The "internal standard" method ratios all signals in the standard and samples to the internal standard signal to correct for sensitivity with time. This comparison showed:

(1) Internal standardization was better two-thirds of the time.

(2) Most of the internal normalization data is good to 10%.

(3) Shifts in instrument sensitivity are mass dependent with the largest shifts occurring at lower masses.

(4) Internal standards methods should use 3 or 4 elements evenly spaced across the mass scale.

Instrumentation Affecting ICP-MS Performance

New alignment jigs and a complete realignment from torch to multiplier has resulted in a 3 to 5 fold improvement in instrument sensitivity. We are presently obtaining $>3x10^6$ cps for 1 ppm (100% isotope) of solution for most elements above mass 50 amu. Photon background is 10 to 20 cps. This translates into both lower detection limits and better counting statistics. A new MCA has been installed with double the channels. The new unit gives higher mass resolution on a full mass scan, better precision, and solves the instrument "lock-up" problem that was occurring when data was transferred between the old MCA and the computer. The much shorter dead time found with the new system permits higher count rates for a given dead time error than the original system.

23. Applications of ICP/MS Detection with Sample Introduction by Flow Injection and Liquid Chromatography

D.S. Bushee and J.R. Moody

The excellent sensitivity and selectivity of the inductively coupled plasma/mass spectrometer (ICP/MS) have been used to advantage in combination with flow injection (FI) and liquid chromatographic (LC) methods of sample introduction. Flow injection analysis provides total metal information which compliments the species specific data obtained from chromatographic analysis. Chromatography can be used to separate the various species of the same element as well as to isolate interferences from the element of interest in complex samples. We have coupled a liquid chromatograph to an inductively coupled plasma/mass spectrometer to obtain both speciation and isolation of elements.

Thimerosal (sodium ethylmercurithiosalicylate) is a mercury containing bactericide used in a number of biological products. The LC/ICP/MS method has been used to investigate the stability of this preservative in a series of injectable solutions and vaccines obtained from the Food and Drug Administration. These include two Lots of Diluent (of different ages), a Lot of Tetanus Toxoid Adsorbed Vaccine and an Influenza Vaccine. Stoppers from the sample bottles, as well as unused, "blank" stoppers were extracted and their total mercury content determined by FI/ICP/MS.

The nominal mercury content for all the samples was 49.6 μg/mL as mercury (100 g/mL as thimerosal). The manufacturers quality control specifies that a lot is acceptable if the thimerosal levels are within ± 5 μg/mL Hg of this level. In each case, FI results agreed with the results obtained by LC, indicating that all mercury species present were accounted for by LC-ICP/MS. The Influenza Vaccine showed a significant loss of thimerosal, almost 50% of the expected level. This loss was traced to the stopper, which contained a substantial quantity of mercury. Qualitative analysis of the newer diluent and the Tetanus and Influenza Vaccine reveal no degradation products. Chromatograms of the year old diluent contain a peak which could not be identified, but which represents a very minor constituent.

In addition, the multielement capabilities of the LC-ICP/MS method have been investigated with the determination of rare earth elements (REE) in NIST Fly Ash SRM 1633a. The REE concentration patterns in fly ash samples can be used to determine whether its source is an oil-fired or coal-fired power plant. In this case, the LC separates the rare earth isobars from each in a ten minute scheme. The detection limits for the REE by LC-ICP/MS are in the sub-ppb range and the response is linear over four orders of magnitude. This technique promises to reduce the time required for analysis by a factor of ten compared to the present technique. Results obtained on SRM 1633a compare favorably to reference values obtained by neutron activation analysis. Future experiments will be done combining isotope dilution with LC-ICP/MS to investigate improvements in precision and accuracy that can be achieved by combining isotope dilution with LC-ICP/MS for fly ash analysis.

24. Automated Mass Spectrometers for Inorganic Analysis

I.L. Barnes and J.W. Gramlich

Thermal ionization mass spectrometers are now produced with many features for automated, high precision isotope ratio measurements. To investigate the advantages of these features, we obtained a new mass spectrometer commercially produced by the Finnigan-MAT Corporation as a Model 261. The instrument contains an automated source region with a turret loading device that permits the loading of up to 13 samples at one time for sequential analysis under computer control. The instrument was also constructed using a new ion optical system called "stigmatic" or non-normal geometry which gives twice the dispersion of equivalent size normal geometry systems. The particular advantage gained is the room to put multiple collectors in a instrument of reasonable dimensions. In our instrument, seven Faraday collectors and one electron multiplier are installed. A further advantage of the non-normal optical system is that focussing is obtained in the vertical or "Z" direction with the result that increased numbers of ions are obtained at the collector.

After a period of adapting previously developed NIST methods to the software and hardware of the new instrument, experiments were designed to test the new features and to compare them with results obtained using the conventional, but highly developed, NIST mass spectrometers. A summary of the experience to date in several areas is given here. For those elements which normally exhibit low mass fractionation or for those with high sensitivity, where small samples can be mounted on the filament, the automated source performs extremely well. In several cases, up to 26 samples were analyzed in one continuous period. Examples of this kind of analysis are neodymium, samarium and strontium, where isotopic ratios for a large number of samples were measured with high precision. However, for elements where ionization is more difficult or very stable temperature is required (for example, with lead), control over the heating pattern by an operator still gives better results and is essential for the highest precision. Under all circumstances, the use of multiple collectors is a major advantage. High precision data was collected during times when the signals from the sample were so unstable that the analysis would have been aborted using a conventional instrument. The multiple collector system also allowed the analysis of very small samples. In one case, ratios of 6 pg of neodymium were measured with a precision of 4 ppm.

The most recent major work consisted of the measurement of the isotopic ratios of several hundred samples of nickel for the determination of the atomic weight of this element. The same samples were also measured on a conventional NIST mass spectrometer. A comparison of the data indicated that for samples and standards of near normal ratios the data from the commercial instruments was only slightly less precise than the data from the NIST instrument. We believe that this may be due to the much smaller magnet gap width of the commercial instrument. For samples with very large isotopic ratios, the NIST developed measurement system produced far better results due to a much wider linear dynamic range in the detection systems. Such is the case where separated nickel isotopic measurements are required for the atomic weight determination.

The net results of these experiments are that the automated, multi-collector instrument has major advantages for the analyses of many kinds of samples and for a number of elements, while for many other frequently analyzed samples, the NIST type mass spectrometer will still give superior results. We have determined that there are a number of areas in which further work will lead to major improvements and we are currently working, in co-operation with the manufacturer, to make these improvements.

25. Investigation of Atomization Processes for High Sensitivity Measurement by RIMS

J.D. Fassett, R.J. Walker, J.C. Travis, T.B. Lucatorto, L. Bengtsson, and S. Mayo

Resonance ionization mass spectrometry (RIMS) is a technique that combines the ability of laser radiation to photoionize gas phase atomic species selectively and efficiently with the mass resolution capabilities of mass spectrometry. We have been using this technique with the production of atomic species from resistively heated filaments. The mismatch between the duty cycles of thermal vaporization and pulsed laser ionization has continued to limit our ultimate measurement sensitivity. Thus, we have investigated laser ablation as an alternative means of vaporization and, at the same time, systematically studied overall measurement efficiencies using thermal vaporization for our current RIMS analytical programs. These programs include the elemental and isotopic measurement of Os and Re in geological materials and the elemental determination of V in high purity semiconductor material.

Laser induced sputtering (desorption or ablation) has been an area of interest for some time. Our initial experiments were directed to the vaporization of Be from a filament substrate. These experiments were very positive in that the time response for atom desorption was very narrow, indicating efficient utilization of the sample. Yet, the common problems with laser ablation from solid substrates were observed: non-linear coupling of the laser radiation with the surface resulting in very large pulse-to-pulse variations of the signal as well as the emission of "chunks" of material. In order to overcome this source of irreproducibility, we developed a thin film ablation technique with a "compact disk" format. The laser completely evaporates a series of 100 μm spots from a rotating quartz disk substrate. For a 50 angstrom thick film, approximately 10^{12} atoms/spot are evaporated. The thin films are formed by co-sputtering a suitable matrix material with the analyte onto the quartz substrate. In principle, with proper geometric overlap, about 1 in 20 of the evaporated atoms will be interrogated by the RIMS laser. This sampling utilization efficiency is probably close to the maximum achievable using pulsed RIMS.

The initial efforts with the compact disk have been directed at finding matrix materials and co-sputtering techniques which produce the maximum sensitivity. The matrix materials studied to date are Pt, Ta, C, Ag, Zn, and a Ni alloy. The thin film was created in each case by argon ion sputtering from a solid target using a planar magnetron plasma. Impurity elements such as Pb, Sn, In, Ni, Mn Mg and Y in the matrices were used to estimate the overall sensitivity of the technique. All experiments were done using a Nd:YAG laser for ablation. To date, both the sensitivity of the method and the shot-to-shot reproducibility have been far from theory. The observed sensitivities are in the ppm range instead of the expected ppb range. We have demonstrated that the ionization associated with the high temperature produced is a significant problem, especially for matrices with high vapor pressures and low ionization potentials. Using a Zn matrix, an ablation laser with longer pulse duration, should reduce this effect. These changes are presently being studied.

Our laboratory has become world reknown for the application of RIMS to the determination of Re and Os concentrations (through isotope dilution) and Os isotopic compositions of chemically purified separates from geologic samples. We have utilized a pulsed, thermal filament to increase the sample utilization efficiency. We have previously estimated a 100-fold improvement in efficiency relative to a continuously heated filament by measuring the emission of Ta atoms from the filament. However, Os emission from the filament is much slower and indicates only a factor of 10- to 20-fold improvement in sensitivity for this analyte. We have considered two explanations for this phenomenon. The first explanation is related to the differences in the heat of sublimation of the two substances. The second explanation is that Os forms a metal solution with the bulk Ta filament, and the Os emission is limited by the rate of diffusion from the bulk to the surface of the filament. Despite the sample which is lost (10^4 times that measured) because of the low laser duty cycle, the pg sensitivity for isotopic analysis of Os has proven sufficient for a number of different studies, completed and ongoing.

Our newest analytical effort with RIMS has been its application to the characterization of high-purity semiconductor material. There are two issues of sensitivity that we are addressing, trace analysis and microanalysis. We have demonstrated ppb sensitivities in the bulk analysis of silicon. We are presently adapting methods to do controlled stripping of thin surface layers, which will then be subsequently analyzed using isotope dilution. Measurement of pg (or less) of impurities in micrograms of sample is the planned goal. We have chosen to develop our method with the determination of vanadium because transition metal impurities are of importance and because RIMS is particularly well suited to the V measurement--the selectivity of the ionization process is critical for success.

We have studied the ionization process for vanadium and compared the measurement sensitivity with thermal ionization. The Saha-Langmuir relationship predicts that the ratio of ionic species to atomic species of V emitted from a rhenium filament at 1342 K is 3.0×10^{-6}. The duty cycle loss factor calculated for RIMS is 1.3×10^{4}. Thus, theory predicts that RIMS is 25 times more sensitive than thermal ionization for these conditions. We have made measurements of thermal ions and photoions that are generated from the same sample on a rhenium filament. The ratio of signals, RI:TI, ranged from 23 (1350 K, 24 ions/s, RI) to 2.1 (1540 K, 38000 ions/s, RI) which is qualitatively in agreement with theory. An important point is that the two techniques are comparable in sensitivity despite the duty cycle losses of resonance ionization. In fact, the RIMS measurements have an important advantage relative to thermal ionization in that the titanium and chromium backgrounds need not be monitored, and corrections need not be made for these interferences. Thus, even with today's lasers and unpulsed sources of atoms, RIMS has analytical advantages in inorganic mass spectrometry for selected, and important, problems.

C. Outputs and Interactions
(Inorganic Analytical Research Division)

1. Publications

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Wu, Y.C., Koch, W.F., Hamer, W.J., and Kay, R.L., "A Review on the Electrolytic Conductance Standards," J. Soln. Chem. 16(12), 985-997 (1987).

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Zeisler, R. and Becker, D.A., "Determination of Zinc in a Monel Alloy by Compton Suppression Spectrometry," Trans. Am. Nucl. Soc. 55, 175, (1987).

Zeisler, R., Stone, S.F., and Sanders, R.W., "Sequential Determination of Biological and Pollutant Elements in Marine Bivalves," Anal. Chem., (in press).

Zeisler, R., Greenberg, R.R., and Stone, S.F., "Radiochemical and Instrumental Neutron Activation Analysis Procedures for the Determination of Low Level Trace Elements in Human Livers," J. Radioanal. Nucl. Chem. (1987), (in press).

Zeisler, R., Greenberg, R.R., Stone, S.F., and Sullivan, T.M., "Selenium Determinations for the Assessment of Sample Stability in Specimen Banking," Trans. Am. Nucl. Soc. 56, 153-154 (1988).

Zeisler, R. and Greenberg, R.R., "Determination of Baseline Platinum Levels in Biological Materials," J. Trace Elem. Electrolytes Health Dis. (1988), (in press).

Zeisler, R., Greenberg, R. R., and Stone, S. F., The Determination of Trace Elements in Human Livers, in Progress in Environmental Specimen Banking, NBS Spec. Publ. 740, U. S. Government Printing Office, Washington, DC, 82-90 (1988).

2. Talks

Barnes, I.L., Trace Element Analyses - State of the Art., Science Awareness Day, Prince Georges Community College, November 10, 1988. Invited

Barnes, I.L., The Development of High Precision Mass Spectrometry, Symposium on Elemental and Isotope Analyses by Mass Spectrometry, 36th ASMS Conference on Mass Spectrometry and Allied Topics, San Francisco, June 5 - 10, 1988. Invited

Barnes, I.L., Experiences with an Automated, Multi-collector Mass Spectrometer, Workshop on "Isotope Ratio MS: A Look to the Future", 36th ASMS Conference on Mass Spectrometry and Allied Topics, San Francisco, June 5 - 10, 1988. Invited

Barnes, I.L., A Redetermination of the Absolute Abundance Ratios and the Atomic Weight of a Reference Sample of Strontium, (T.J. Murphy and K.R. Eberhardt, co-authors), 11th International Mass Spectrometry Conference, Bordeaux, France, August 29 - September 2, 1988.

Barnes, I.L., A Redetermination of the Absolute Abundance Ratios and the Atomic Weight of a Reference Sample of Strontium, (T.J. Murphy and K.R. Eberhardt, co-authors), Central Bureau for Nuclear Measurements, Geel, Belgium, September 5, 1988. Invited

Beary, E.S. and Paulsen, P.J., "Trace Metal Determinations in NBS Bovine Serum Using ICP/MS Isotope Dilution," 30th Rocky Mountain Conference, Denver, Colorado, July 1988.

Beary, E.S. and Paulsen, P.J., "Trace Element Determinations in Bovine Serum Using Stable Isotopic Dilution," 30th Rocky Mountain Conf., Denver, CO, July 1988.

Becker, P.R., Koster, B.J., Zeisler, R., and Wise, S.A., "The Alaskan Marine Mammal Tissue Archival Program - Development of a Contaminant Monitoring Resource," 11th U.S. German Seminar of State and Planning on Environmental Specimen Banking, Bayreuth, FRG, May 2, 1988. Invited

Becker, D.A., "Determinationo f Zinc in a Monel Alloy by compton Supression Spectrometry," American Nuclear Society Winter Meeting, Los Angeles, November 16, 1987. Invited

Becker, D.A., "Fast-Neutron INAA: Nickel Sensitivities and Fluence Varaitions at Three Reactors," American Nucler Society Symposium, San Diego, CA, June 15, 1988. Invited

Becker, D.A., "Neutron Activation Analysis: A Unique Tool for Reference Material Certification," Czechoslovak Spectroscopy Society Conference, Ceske Budejovice, Czechoslovakia, June 23, 1988. Invited

Becker, D.A., "Neutron Activation Analysis at NBS," Nuclear Research Institute, Rez, Czechoslovakia, June 24, 1988.

Becker, D.A., "Accuracy and Precision in NAA at NBS," International Atomic Energy AGency, Seibersdorf Laboratory, Seibersdorf, Austria, July 5, 1988.

Bengtsson L., Travis, J.C., Fassett, J.D., Kreider, K., Lucatorto, T.B., and Brown, L., "Atomization by Laser Ablation of Thin Films for Pulsed RIMS," 4th RIS Symposium, Gaithersburg, MD, April 12, 1988.

Downing, R.G., "Neutron Depth Profiling: Current Developments of the Technique in the United States," American Nuclear Society Conference on Industrial Radiation and Radioisotope Measurement Applications, Pinehurst, N.C., September 6, 1988. Invited

Downing, R.G., "On Neutron Depth Profiling," Radiation Reactor Division Staff Seminar, NBS, August 4, 1988.

Epler, K.S., O'Haver, T.C., and Turk, G.C., "Laser-Enhanced Ionization Spectroscopy for Biological Trace Metal Analysis," North American Chemical Conference, Toronto, Canada, June 8, 1988. Invited

Epler, K.S., O'Haver, T.C., Turk, G.C., and MacCrehan, W.A., "Applications of Liquid Chromatography-Laser Enhanced Ionization Spectroscopy," FACSS '88', Boston, October 31, 1988.

Epstein, M.S., "Computer Communication and Information Services for the Scientist," Department of Chemistry and Biochemistry Seminar, University of Maryland, College Park, MD, October 1987. Invited

Epstein, M.S., Watters, R.L., Jr., Kingston, H.M., and Miller-Ihli, N.M., "Successful Atomic Spectrometric Determinations", SAS Short Course, Detroit, MI, October 3-4, 1987. Invited

Epstein, M.S., Watterls, R.L., Jr., Kingston, H.M., and Miller-Ihli, N.M., "Successful Atomic Spectrometric Determinations," SAS Short Course, New Orleans, LA, February 20-12, 1988. Invited.

Ewing, K., Rains, T.C., Paulsen, P.J., and Beary, E.S., "Purification and Analysis of Fluoride Raw Materials at Sub-ppb Levels," Japan, April 1988.

Fassett, J.D., Inn, K.G.W., and Watters, R.L., Jr., "Development of the NBS Beryllium Isotopic Standard Reference Material," 4th RIS Symposium, Gaithersburg, MD, April 12, 1988.

Fassett, J.D. and Travis, J.C., "Laser RIMS--From Conception to Reality," 1988 Gordon Research Conference on Analytical Chemistry, New Hampton, NH, August 8, 1988.

Fleming, R.F., "Advances with Neutron Beam Techniques," Symposium on Accuracy in Trace Analysis, Gaithersburg, MD, September 30, 1987.

Fleming, R.F., "The Medium Flux Reactor as a Research Tool in Materials Analysis," McMaster University, Hamilton, Ontario, Canada, December 21, 1987.

Fleming, R.F., "Elemental Analysis Using Neutron Beam Techniques," Indo-US Workshop on Advanced Techniques for Microstructural Characterization," Bombay, India, January 13, 1988.

Fleming, R.F., "Elemental Analysis with Neutron Beams," Indira Gandhi Centre for Atomic Research," Kalpakkam, India, January 19, 1988.

Fleming, R.F., "Advances with Neutron Beam Techniques," Chemistry Department Seminar, University of Maryland, College Park, MD, February 26, 1988.

Fleming, R.F., "Neutron Depth Profiling with Cold Neutrons," NBS Workshop on Microstructure and Macromolecular Research with Cold Neutrons, Gaithersburg, MD, April 21, 1988.

Fleming, R.F., "Study of Polymers with Neutron Depth Profiling," Staff seminar, Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts, May 6, 1988.

Fleming, R. F., "Neutron Interrogation and Diagnostics," Symposium on the Research Potential of the Georgia Tech Reactor, Georgia Institute of Technology, Atlanta, Georgia, May 12, 1988.

Fleming, R.F., "A Nuclear Engineering Approach to Neutron Activation Analysis," Nuclear Engineering Department Seminar, University of Michigan, Ann Arbor, Michigan, July 26, 1988.

Greenberg, R.R., Zeisler, R.L, and Malozowski, S., "Investigation of Natural Chromium Levels in Human Blood," 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, FRG, April 15, 1988.

Greenberg, R.R., Zeisler, R., Kingston, H.M., and Sullivan, T.M., "Neutron Activation Analysis of the NBS Bovine Serum Standard Reference Material Using Chemical Separations," Third International Symposium on Biological Reference Materials, Bayreuth, FRG, May 6, 1988.

Greenberg, R.R. and Inn, K.G.W., "Determination of Uranium-238 in Environmental radioactivity Standard Reference Materials by Instrumental Neutron Activation Analysis," Thirty-third Annual Conf. on Bioassay, Analytical and Environmental Radiochemistry, Berkeley, CA, October 7, 1987.

Greenberg, R.R., "Evaluation of Precision and Accuracy of Selenium Measurements in Biological Materials Using Neutron Activation Analysis," American Nuclear Society Summer Meeting, San Diego, CA, June 14, 1988. Invited

Greenberg, R.R., Zeisler, R., and Malozowski, S., "Investigation of Natural Chromium Levels in Human Blood," 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, FRG, April 15, 1988.

Inn, K.G.W., Fassett, J.D., Coursey, B.M., Walker, R.L., and Raman, S., "Development of the NBS Beryllium Isotopic Standard Reference Material," DOE Workshop on Advanced Laser Technology for Chemical Measurements, NBS, Gaithersburg, MD, November 5, 1987.

Iyengar, G.V., Clarke, W.B., Downing, R.G., and Tanner, J.T., "Boron and Lithium in Biological and Dietary Materials," 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, FRG, April 15-18, 1988.

Iyengar, G.V. and Wolf, W.T., "Multi-Purpose Biological RMs," Third International Symposium on Biological Reference Materials, Bayreuth, FRG, May 4-7, 1988.

Iyengar, G.V., "Nutritional Chemistry of Chromium," Symposium on Chromium Paradox in Modern Life sponsored by Association of Government Toxicologists, NIH, Bethesda, MD, May 23-24, 1988. Invited

Iyengar, G.V., "Total Quality Control Procedures for Biological Trace Element Research Studies," Expert Panel on Quality Control, International Conference on Trace Elements in Health and Disease, Odense, Denmark, August 16-21, 1987. Invited

Iyengar, G.V., Wolf, W.R., and Tanner, J.T., "USDA-FDA-NBS Project in the Coordinated Research Program on Human Dietary Intake of Minor and Trace Elements," Third Conference for Federally supported Human Nutritional Research Units, NIH, Bethesda, MD, February 24-25, 1987. Invited

Iyengar, G.V., "ICRP Reference Man Update," IV Task Group Meeting of the International Commission on Radiological Protection, Paris, June 26-July 1, 1988.

Iyengar, G.V., "Nutritional Chemistry of Chromium," Symposium on Chromium Paradox in Modern Life Sponsored by Association of Government Toxicologists, NIH, Bethesda, MD, May 23-24, 1988.

Iyengar, G.V. and Woittiez, J.R.W., "Trace Elements in Human Clinical Specimens," An Evaluation of Literature Data to Identify Reference Values, 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, April 15-18, 1988.

Iyengar, G.V., Wolf, W.R., Tanner, J.T., and Zeisler, R., Working Report on investigations carried out during 1987-1988, "IAEA Coordinated Research Program on Human Daily Dietary Intake of Nutritionally Important Trace Elements," Meeting of the Analysts, Vienna, April 9-10, 1988.

Iyengar, G.V., "ICRP Reference Man- an Update," III Task Group Meeting of the International Commission on Radiological Protection, ORNL, Oak Ridge, Tennessee, December 2-4, 1987.

Iyengar, G.V., Wolf, W.R., Tanner, J.T., and Zeisler, R., Working Report on investigations carried out During 1986-1987, "IAEA Coordinated Research Program on Human Daily Dietary Intake of Nutritionally Important Trace Elements," III Research Coordination Meeting, Kona, Hawaii, April 6-11, 1987.

Iyengar, G.V., "Radiochemical Separations for Trace Elements in Total Diets," International Conference on Methods and Applications of Radioanalytical Chemistry, ANS Topical Conf., Kona, Hawaii, April 5-10, 1987.

Iyengar, G.V., "ICRP Reference Man- an Update," II Task Group Meeting of the International Commission on Radiological Protection, Chiba, Japan, March 9-14, 1987.

Iyengar, G.V., Clarke, W.B., Downing, R.G., and Tanner, J.T., "Boron and Lithium in Biological and Dietary Materials," 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, FRG, April 16, 1988.

Iyengar, G.V. and Wolf, W.R., "Multi-Purpose Biological RMs," Third International Symposium on Biological Reference Materials, Bayreuth, FRG, May 4, 1988.

Jassie, L.B. and Kingston, H.M., "Some Aspects of the Chemistry of Acid Dissolution in a Microwave System," 30th ORNL-DOE Energy Technology Conference, October, 20-22, 1987.

"The Development and use of Fast Microwave Acid Sample Decomposition for Elemental Analysis", Beijing Conference and Exhibition on Instrumental Analysis, Beijing, Peoples Republic of China, October 20, 1987. Invited

"Development of a computer-Controlled Robot System for Analytical Separations by Column Chromatography", Beijing Conference and Exhibition on Instrumental Analysis, Beijing, Peoples Republic of China, October 21, 1987. Invited

"Microwave Energy for Sample Preparation", Shanghai Institute of Testing Technology, Shanghai, People's Republic of China, November 2, 1987. Invited

"Laboratory Robotics", Shanghai Institute of Testing Technology, Shanghai, People's Republic of China, November 2, 1987. Invited

"Microwave Assisted Digestive Techniques and Chemical Robotics," EPA EMSL - Cincinnati, Cincinnati, OH, December 2, 1987. Invited

"Microwave Assisted Sample Decomposition for Trace Analysis", Short course, 1988 Winter Conference on Plasma Spectrochemistry, San Diego, CA, January 2, 1988. Invited

"Microwave Assisted Decomposition of Soils", part of a short course on Sample Preparation at the 1988 winter conference on Plasma Spectro-chemistry, San Diego, CA, January 2, 1988. Invited

Panel Discussion: "Solving Difficult Problems with Microwave Assisted Sample Decomposition", 1988 Winter Conference on Plasma Spectrochemistry, San Diego, CA, January 6, 1988. Invited

"The Use of Microwave Technology for Sample Digestion and Preparation", Phillips Petroleum Company, Bartlesville, OK, February 19, 1988. Invited

"Microwave Energy for Sample Preparation and Robotics for Analytical Analysis", Arco Oil and Gas Company, Plano, TX, February 24, 1988. Invited

"Microwave Acid Sample Decomposition for Elemental Analysis", Pittsburgh Conference, New Orleans, LA, February 26, 1988.

EPA Seminar: "Computer Controlled Laboratory Robotics and Microwave Sample Preparation", Las Vegas, NV, April 4, 1988. Invited

Kingston, H.M. and Jassie, L.B., "Fundamental Relationships in Acid Decomposition of Environmental Samples for Elemental Analysis using Microwave Energy," presented at the Symposium on Microwave Processing of Materials, paper #M5.1, Reno, NV, April 5-8.

"High Temperature Microwave Sample Decomposition for Elemental Analysis", Materials Research Society, Reno, NV, April 7, 1988. Invited

Kingston, H.M. and Jassie, L.B., "High Temperature and Pressure Acid Decomposition of Materials in a Microwave System," presented to a joint ASTM D-34 and D-19 committee meeting, Toronto, Ontario, May 17, 1988.

"Fundamentals of Microwave Sample Preparation: With Practicum" Training Course of the Society for German Chemists, No. 349/88, Sample Preparation for Trace Analysis for Trace Elements and Radionuclides, Kernforschungsanlage, Centeral Department for Chemical Analysis, Julich GmbH, West Germany, May 19, 1988. Invited

"Laboratory Robotics", Meeting of EPA Regional Laboratory Directors and Branch Chiefs, Mayflower Park Hotel, Seattle, WA, June 14, 1988. Invited

"Microwave Sample Preparation for Environmental Testing", Meeting of EPA Regional Laboratory Directors and Branch Chiefs, Mayflower Park Hotel, Seattle, WA, June 14, 1988. Invited

Kingston, H.M. and Jassie, L.B. "Fundamental Relationships in Acid Decomposition of Environmental Samples for Elemental Analysis Using Microwave Energy" EPA OSW Symposium on: Waste Testing and Quality Assurance, Westin Hotel, Washington DC, July 13, 1988.

Koch, W.F., "Ion Chromatography: Trace Analysis," Department of Chemistry Distinguished Lecturer Series, Drury College, Springfield, MO, December 7, 1987. Invited

Koch, W.F., "Reference Materials for Sodium and Potassium: National Bureau of Standards Efforts," American Association for Clinical Chemistry, 40th National Meeting, New Orleans, LA., July 25, 1988. Invited

Koch, W.F., "Development of a Reference Material for ISE Measurements of Sodium and Potassium," 10th Meeting of the European Working Group on Ion Selective Electrodes, Stresa, Italy, September 23, 1988. Invited

Koster, B.J., Wise, S.A., and Zeisler R.L., "Technical Improvements in the Operation of the U. S. National Biomonitoring Specimen Bank Facility," 11th U.S. German Seminar of State and Planning on Environmental Specimen Banking, Bayreuth, FRG, May 3, 1988. Invited

Lindstrom, R.M., "Analytical Standards and Silicon Analysis," International Energy Agency Consultants' Meeting on the Need for Intercomparison and Reference Materials for Characterization of Silicon, National Bureau of Standards, Gaithersburg, MD, October 2, 1987. Invited

Lindstrom, R.M., "Prompt-Gamma Activation Analysis," Test, Research, and Training Reactors Meeting, National Bureau of Standards, Gaithersburg, MD, October 15, 1987. Invited

Lindstrom, R.M., "Cold Neutron Facility at the National Bureau of Standards," Department of Nuclear Engineering, University of Illinois, Urbana, May 9, 1988. Invited

Lindstrom, R.M., "Analysis Using Neutron Beams at NBS," Environmental and Medical Sciences Division, United Kingdom Atomic Energy Authority, Harwell, U.K., June 7, 1988. Invited

Lindstrom, R.M., "Measurement of Superconductor Stoichiometry by Prompt and Delayed Neutron Activation," American Nuclear Society Annual Meeting, San Diego, CA, June 16, 1988.

Lindstrom, R.M., "Stoichiometry Measurement by Neutron Activation," Third NBS Superconductivity Program Review, Boulder, CO, July 15, 1988.

Lindstrom, R.M., "Neutron Microprobe: Prospects and Potential Applications," Microbeam Analysis Society - Electron Microscopy Society of America Joint Meeting Milwaukee, Wisconsin, August 10, 1988. Invited

Lindstrom, R.M., "Neutron Activation Analysis in Electronic Technology," Symposium on Diagnostic Techniques for Semiconductor Materials and Devices, 174th Meeting of the Electrochemical Society, Chicago, Ill., October 12, 1988. Invited

Lucatorto, T.B., Travis, J.C., Fassett, J.D., Clark, C.W., and Brown, L., "Enhanced Isotope Abundance Sensitivity and Sample Utilization Efficiency in Pulsed RIMS," DOE Workshop on Advanced Laser Technology for Chemical Measurements, NBS, Gaithersburg, MD, November 5, 1987.

Marinenko, G., "Constant Current Coulometry - A Versatile High - Precision Titration Technique," International Symposium on Titration Techniques, Lund, Sweden, June 13, 1987. Invited

Mills, C.F., Golden, M., and Iyengar, G.V., "Trace Element Nutritional Problems in the Developing Countries," International Conference on Trace Elements in the Developing Countries, Karachi, Pakistan, February 6-10, 1987. Invited

Moody, J.R., Paulsen, P.J., Beary, E.S., and Bushee, D.S., "Inductively Coupled Plasma - Mass Spectrometric Analysis of Ultrapure HF," 1st International Conference on Plasma Source Mass Spectrometry Durham University, UK, September 1988.

Moody, J.R., Paulsen, P.J., Beary, E.S., and Bushee, D.S., "ICP-MS Analysis of Ultrapure HF," First International conference on Plasma Source Mass Spectrometry; Durham Univ. England, September 1988.

Norris, J.A., "Major Minor and Trace Elemental Analysis as Seen by an Instrumentalist:, Iron and Steel Chemists' Association Annual Meeting, Pittsburg, PA, October 1987.

Palmieri, M. and Fritz, J.S., "Detection of Metal Ions by Liquid Chromatographic Separation of Their 1,3-Dimethyl-4-Acetyl-2-Pyrazolin-5-one Chelates," HPLC'88, Washington DC June 1988.

Paulsen, P.J., "Techniques for SSMS Isotope Dilution Analysis of Standard Reference Materials," Central Bureau for Nuclear Measurements Commission of the European Communities, Geel, Belgium, July 1988. Invited

Paulsen, P.J., "ICP-MS Analysis of Trace Elements Using Isotope Dilution and/or External Standardization," Central Bureau for Nuclear Measurements Commission of the European Communities, Geel, Belgium, July 1988. Invited

Paulsen, P.J., Moody, J.R., Beary, E.S., and Bushee, D.S., "ICP-MS: Application to the Analysis of Ultrapure Acids," University of Maryland, Analytical Chemistry Seminar, College Park, MD, October 23, 1987. Invited

Paulsen, P.J., Beary, E.S., and Bushee, D.S., "Stable Isotope Dilution Analysis of Oyster Tissue Using ICP-MS," 11th International Mass Spectrometry Conference, Bordeaux, France, August 1988.

Rains, T.C., Paulsen, P.J., Beary, E.S., and Turk, G., "New Analytical Techniques for Fluoride Materials," Fiber Optics Conference, McLean, VA, March 1988.

Rains, T.C., Paulsen, P.J., Beary, E.S., Turk, G., and Ewing, K., "Purification and Analysis of Fluoride Raw Materials at Sub ppb Levels," Rains, T.C., "The Art of Sample Preparation for Spectrochemical Analysis," FACSS Workshop, Detroit, MI, October 6, 1987. Invited

Rains, T.C., "The Art of Sample Preparation," Beijing Reagent Chemical Institute, Beijing, China, October 15, 1987. Invited

Rains, T.C., "Chemical Interference in Atomic Absorption Spectrometry and Ways to Alleviate Them," Beijing Reagent Chemical Institute, Beijing, China, October 17, 1987. Invited

Rains, T.C., "New Innovation in AAS," Beijing Reagent Chemical Institute, Beijing China, October 17, 1987. Invited

Rains, T.C. and Syty, A., "Determination of Trace Elements Species by HPLC/AAS in Environmental Samples," 2nd Beijing Conference and Exhibition on Instruments Analysis, Beijing China, October 20, 1987.

Rains, T.C., "Research Atomic Absorption and Emission Spectrometry at NBS," National Spectroscopy Society of China, Beijing, China, October 21, 1987. Invited

Rains, T.C., "Trace Analysis in Ultra Pure Materials," Beijing Reagent Chemical Institute, Beijing, China, October 22, 1987.

Rains, T.C., "The Art of Sample Preparation" and "New Innovation in Atomic Spectroscopy," Northwest Nonferrous Geological Institute, Xian, China, October 26, 1987. Invited

Rains, T.C., "Interference in Atomic Spectroscopy" and "Quality Assurance," Northwestern Nonferrous Geological Institute, Xian, China, October 27, 1987. Invited

Rains, T.C., "The Art of Sample Preparation," Tong Ji University, Shanghai, China, October 28, 1987. Invited

Rains, T.C., "Trace Element Determination by AAS and FES," Tong Ji University, Shanghai, China, October 29, 1987. Invited

Rains, T.C., "Interference in AAS," "Calibration of AAS Instrumentation," and "Quality Assurance in the Analytical Laboratory," Tong Ji University, Shanghai, China, October 30, 1987. Invited

Rains, T.C., "The Art of Sample Preparation" and "Trace Elemental Analysis in Environmental Media," Shanghai Institute of Ceramics, Shanghai, China, October 31, 1987. Invited

Rains, T.C., "The Art of Sample Preparation," and "Trace Elemental Analysis in Environmental Media," Thongsham University, Guangzhon, China, November 2, 1987. Invited

Rains, T.C., "New Innovation in Atomic Spectroscopy," and "Why Quality Assurance," Thongshan University, Guangzhon, China, November 3, 1987. Invited

Rains, T.C. and Taylor, H.E., "Analytical Atomic Spectrometry: Absorption, Emission and Mass," ACS Short Course, New Orleans, LA, February 19-21, 1988. Invited

Rains, T.C., "2nd Annual Trace Analysis for Environmental and Fuel Related Materials," Short Course, Florida Power, Tampa, FL, March 18, 1988. Invited

Rains, T.C., "Art of Sample Preparation" and "Quality Assurance in the Modern Laboratory," Paffenbarger Research Center, Bldg. 224, NBS, May 10, 1988. Invited

Rains, T.C., "Improved Precision and Accuracy in an Analyses by Electrothermal Atomic Absorption Spectrometry," Gordon Research Conference on Analytical Chemistry, New Hampton School, NH, August 12, 1988. Invited

Rains, T.C. and Taylor, H.E., "Analytical Atomic Spectrometry: Absorption, Emission and Mass," ACS Short Course, Los Angeles, CA, September 23-25, 1988. Invited

Settle, F.A. and Pleva, M., "An Expert-Database System for Surface Analysis," Pittsburgh Conference, New Orleans, LA February 25, 1988. Invited

Settle, F.A., "Applications of Expert Systems to Chemical Problems," University of North Carolina at Wilmington, Wilmington, NC, April 14, 1988.

Settle F.A. and Kingston, H.M., "An Expert System for Sample Preparation," Third Chemical Congress of North America, Toronto, Canada, June 9, 1988.

Settle, F.A., Altman, L., McClintock, D., and Pleva M., "The Role of Expert Systems in Chemical Education," Third Chemical Congress of North America, Toronto, Canada, June 7, 1988.

Stone, S.F., Zeisler, R., and Gordon, G.E., "Quantitative Determination of Proteins Using Polyacrylamide Gel Electrophoresis and Neutron Activation," 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, FRG, April 18, 1988.

Stone, S.F., Koster, B.J., and Zeisler, R., "Inorganic Analyses of Marine Specimens from the National Oceanic and Atmospheric Administration's National Status and Trends Program," 11th U.S. German Seminar of State and Planning on Environmental Specimen Banking, Bayreuth, FRG, May 2, 1988. Invited

Stone, S.F., Zeisler, R., and Koster, B.J., "Neutron Activation Analysis of Major, Minor, and Trace Elements in Marine Sediments," ANS Annual Meeting, San Diego, CA, June 16, 1988.

Tanner, J.T., Smith, J.S., Angyal, G., Defibaugh, P.W., Villalobos, M.C., Bueno, M. P., Iyengar, G. V., Wolf, W. R., and Zeisler, R., "Organic Nutrient Standards," Accuracy in Trace Analysis, Accomplishments, Goals, Challenges, NBS, Gaithersburg, September 28-October 1, 1987.

Travis, J., "Resonance Ionization Mass Spectrometry for Ultra-Sensitive Determination of Isotope Ratios," V. M. Goldschmidt Conference (Geochemical Society), Baltimore, MD, May 13, 1988.

Travis, J., "Developing the Ultimate Analytical Potential of Resonance Ionization Mass Spectrometry," 41st Annual Summer Symposium on Analytical Chemistry, Stanford University, Palo Alto, CA, June 28, 1988.

Turk, G.C., Kingston, H.M., Epler, K.S., and O'Haver, T.C., "Applications of Laser-Enhanced Ionization Spectroscopy," FACSS XIV, Detroit, MI, October 6, 1987.

Turk, G.C., "Tributyltin Measurements," EPA, Cincinnati, Ohio, December 2, 1987.

Turk, G.C., MacCrehan, W.A., Epler, K.S., and O'Haver, T.C., "Laser-Enhanced Ionization as an Element Specific Detector for Liquid Chromatography, Fourth International Symposium on Resonance Ionization Spectroscopy and Its Applications," Gaithersburg, MD, April 15, 1988.

Turk, G.C., "Fundamentals and Applications of Laser-Enhanced Ionization Spectroscopy," Vancouver/Victoria Section of the Spectroscopy Society of Canada, Vancouver, BC, Canada, April 18, 1988. Invited

Turk, G.C., "Applications of Laser-Enhanced Ionization Spectrometry," Eastern Analytical Symposium, New York City, October 4, 1988. Invited

Turk, G.C., "Simultaneous Measurement of Laser-Indiced Fluorescence and Ionization," FACSS '88', Boston, October 31, 1988.

Turk, G.C., "Fundamentals and Applications of Laser-Enhanced Ionization Spectroscopy," Pacific Northwest Section of the Society for Applied Spectroscopy, Seattle, WA, April 19-20, 1988. Invited

Turk, G.C., "Fundamentals and Applications of Laser-Enhanced Ionization Spectroscopy," Intermountain Section of the Society for Applied Spectroscopy, Idaho Falls, ID, April 21, 1988. Invited

Walker, R.J., Fassett, J.D., and Travis, J.C., "The Use of Resonance Ionization Mass Spectrometry for Measuring the Isotopic Compositions of Rhenium and Osmium Extracted from Silicate Rocks," 4th RIS Symposium, Gaithersburg, MD, April 15, 1988.

Watters, R.L., Jr., Shen, F.H., Newbury, D.E., and Small, J.A., "The Chemical Characterization of Spark Erosion and Spark-Produced Metal Aerosols," Fourteenth Meeting of the Federation of Analytical Spectroscopy Societies, Paper 325, October 5, 1987, Detroit, MI.

Woittiez, J.R.W. and Iyengar, G.V., "Trace Elements in Human Clinical Specimens: An Evaluation of Literature Data to Identify Reference Values," 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, FRG, April 15, 1988.

Woittiez, J.R.W. and Iyengar, G.V., "The Use of NAA in Dietary RM Analysis," Third International Symposium on Biological Reference Materials, Bayreuth, FRG, May 6, 1988.

Wolf, W.R. and Iyengar, G.V., "Mixed Diet RMs for Nutrient Analysis: Preparation of SRM 1548 Total Diet," Third International Symposium on Biological Reference Materials, Bayreuth, FRG, May 6, 1988.

Zeisler, R., Iyengar, G.V., Tanner, J.T., and Wolf, W.R., "Development of Multi-Purpose Reference Materials," Symposium on Accuracy in Trace Analysis - Accomplishments, Goals, Challenges, Gaithersburg, MD, September 29, 1987.

Zeisler, R. and Becker, D.A., "Determination of Zinc in a Monel Alloy by Compton Suppression Spectrometry," ANS Winter Meeting, Los Angeles, CA, November 16, 1987. Invited

Zeisler, R. and Greenberg, R.R., "Determination of Baseline Platinum Levels in Biological Materials," 5th International Workshop on Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, FRG, April 15, 1988.

Zeisler, R., Stone, S.F., Greenberg, R.R., and Sullivan, T.M., "Reanalysis of Banked Human Liver Samples for the Determination of Inorganic Constituents," 11th U.S. German Seminar of State and Planning on Environmental Specimen Banking, Bayreuth, FRG, May 2, 1988. Invited

Zeisler, R., Iyengar, G.V., Tanner, J.R., and Wolf, W.R., "Specimen Banking of U.S. Mixed Total Diets," 11th U.S. German Seminar of State and Planning on Environmental Specimen Banking, Bayreuth, FRG, May 2, 1988. Invited

Zeisler, R. and Wise, S.A., "Long Term Sample Stability - The Key to Specimen Banking," 11th U.S. German Seminar of State and Planning on Environmental Specimen Banking, Bayreuth, FRG, May 3, 1988. Invited

Zeisler, R., Greenberg, R.R., Stone, S.F. and Sullivan, T.M., "Studies on the Long Term Stability of Biological Materials for Trace Elements," Third International Symposium on Biological Reference Materials, Bayreuth, FRG, May 5, 1988.

Zeisler, R., Greenberg, R.R., Stone, S.F., Sullivan, T.M., "Selenium Determinations for the Assessment of Sample Stability in Specimen Banking," ANS Annual Meeting, San Diego, CA, June 14, 1988. Invited

3. Committee Assignments

I. Lynus Barnes

Department of Health and Human Resources, Chemistry Task Force of the National Shellfish Sanitation Program
International Union of Pure and Applied Chemistry,
Commission on Atomic Weights and Isotopic Abundances
Chairman, IUPAC Sub-commission on Isotopic Abundance Measurements
Vice-Chairman, Washington Editorial Review Board

Donald A. Becker

ASTM E-10, Nuclear Technology and Applications
ASTM E-10.05, Nuclear Radiation Metrology
ASTM E-10.05.02, Radionuclide Metrology
ASTM E-10.05.08, Nuclear Environmental Metrology
ASTM E-10.05.10, Neutron Metrology
ASTM D-19, Water
ASTM D-19.01, Statistical Methods
ASTM D-19.02, General Specification and Technical Resources
ASTM D-19.03, Sampling of Water and Water-Formed Deposits, and Surveillance of Water
ASTM D-19.04, Methods of Radiochemical Analysis
ASTM D-19.05, Inorganic Constituents in Water
ASTM D-19.07, Sediments
Chairman, ASTM E-10.05.12, Task Group on Nuclear Methods of Chemical Analysis
ANS, Trace Element Analysis Committee, Biology and Medicine Division
ANS, Activation Analysis Committee, Isotopes and Radiation Division

M. James Blackman

Smithsonian Institution:
Materials Analysis Academic Program Committee
SARCAR Advisory Committee

Extramural Committees:
ASTM E-10.05.12, Task Group on Nuclear Methods of Chemical Analysis

Barry I. Diamondstone
ASTM E-03, Chemical Analysis of Metals
ASTM E-03.1, Ferrous Metals
ASTM E-03.95, Long-Range Planning
ASTM E-03.97, Meetings and Arrangements
ASTM D-34, Waste Disposal

R. Gregory Downing
ASTM E-10.05, Nuclear Methods for Chemical Analysis
ASTM F-01.11, Task Group on Alpha Particle Induced Soft Errors
Center for Analytical Chemistry Colloquium Committee
Inorganic Analytical Research Division Seminar Committee
Organizer and Session Chairman, "Material Characterization Using Neutron Depth Profiling," American Nuclear Society, 1987 Winter Meeting Los Angeles, CA

Michael S. Epstein
ASTM D-19, Water
Advisory Board of Analytical Chemistry (1988-1990)
Course Director, Society of Applied Spectroscopy Course on "Successful Atomic Spectrometric Determinations"
Federation on Analytical Chemistry and Spectroscopy Societies (FACSS-89) Program Committee
Chairman-Elect, Nominating Committee, Society for Applied Spectroscopy (SAS)
Chairman, Outstanding Award Committee, Balitmore-Washington Section of SAS

Ronald F. Fleming
ASTM E-10.05, Nuclear Radiation Metrology
ASTM E-10.07, Radiation Effects on Materials
NSERC Visiting Committee on the McMaster Nuclear Reactor

Robert R. Greenberg
ASTM E-10.05, Nuclear Radiation Metrology
NIST Chemistry Storeroom Committee
ANS, Trace Analysis Committee, Division of Biology and Medicine
Secretary/Treasurer, ANS, Division of Biology and Medicine

G. V. Iyengar
International Commission on Radiological Protection, Task Group on Reference Man
International Union of Pure and Applied Chemistry, Subcommittee on Risk Assessment (SORA)
International Union of Pure and Applied Chemistry, SORA Coordinator for Working Group on Selenium
International Union of Pure and Applied Chemistry, Sub-committee on Quality Assurance and Harmonization
International Scientific Committee, Modern Trends in Activation Analysis
Editorial Board, Science of the Total Environment (U.K.)
Advisory Board, Food Laboratory News Letter (Sweden)

Howard M. Kingston

ASTM C-26.05, Methods of Test
ASTM C-26.07, Waste Materials
IUPAC, Analytical Chemistry Division, Commission V.3, Analytical Nomenclature
Session Chairman, Eastern Analytical Symposium on Microwave Technology
Technical Consultant, Congressional Science and Technology Committee
Chairman, Inorganic Analytical Research Division Seminar Committee

William F. Koch

ASTM D-19, Water
ASTM D-19.02, General Specifications and Technical Resources
ASTM D-19.05, Inorganic Constituents in Water
ASTM D-22, Air
ASTM D-22.06, Atmospheric Deposition
Chairman, ASTM D-22.06.03, Task Group on pH
NIST Child Care Association
National Committee for Clinical Laboratory Standards
American Water Works Association

John K. Langland

Chairman, NBS Electronics Storeroom Committee

Richard M. Lindstrom

NIST Reactor Safety Evaluation Committee
Co-Organizer and Chairman, IAEA Workshop on "The Need for Intercomparison and Reference Materials for Characterization of Silicon," Gaithersburg, October 1988.

Lawrence A. Machlan

ASTM C-26, Nuclear Materials
ASTM C-26.01, Editorial
ASTM C-26.05, Analytical Methods

George Marinenko

The National Capital Section of the Electrochemical Society Counselor, 88/89
ASTM, Committee D-19 Water, Voltammetry Task Group
Chairman, ASTM, Redox Potential Task Group, 1981/88
Chairman, ASTM, pH in Saline Water Task Group, 1981/88
Chairman, ASTM, Chlorine Residuals Task Group, 1981/88

John R. Moody

ASTM D-19, Water
ASTM D-19.05, Inorganic Constitutents in Water
American Chemical Society Committee on Analytical Reagents

John A. Norris

1st Vice Chairman ASTM E-02, Emission Spectroscopy
ASTM E-02.01, Fundamental Practices
ASTM E-02.02, Statistics
ASTM E-02.04, Sampling and Standards
ASTM E-02.05, Copper, Cobalt, Nickel, and High Temperature

ASTM E-02.06, Lead, Tin, Zinc
ASTM E-02.07, Aluminum
ASTM E-02.08, Refractory Metals
ASTM E-02.09, Ferrous
ASTM E-02.13, Terminology
Consultant-Chemists Committee-American Iron and Steel Institute

Kenneth W. Pratt

NIST Research Information Center, Div. 551 Subject Specialist
Inorganic Analytical Research Division Seminar Committee
Division 551 Lunch Bunch organizer, Jan-May 1988
Division 551 High Purity Reagents Committee

Margo D. Palmieri

Washington Chromatography Discussion Group

Theodore C. Rains

Proposal Evaluation Committee for National Science Foundation
Editorial Board of Annual Reports on Analytical Atomic Spectroscopy (The Chemical Society of London) and the Canadian Journal of Spectroscopy, and the Journal of Analtyical Atomic Spectrometry
Subcommittee No. 6 on Methods of Air Sampling and Analysis
ASTM E-02.10, Non-Metallic Materials
ASTM E-02.13, Nomenclature
ASTM D-19, Water
NIH Proposal Evaluation Committee for Instrumentation
Past-Chairman, FACSS Governing Board
Professor-in-Charge, ACS Short Course on Atomic Absorption and Plasma Emission Spectroscopy
Column Editor, Journal of Applied Spectroscopy
Chairman, International Organization for Standardization, Technical Committee 17
Convener of ISO/TC 17/SC1, WG16, Steel and Iron - Determination of Manganese Content - Flame Atomic Absorption Spectrometry

Theresa A. Rush

Inorganic Analytical Research Division Safety Committee

Frank A. Settle

Advisory Board, Journal of Chemical Information and Computer Sciences
Editor of the "Chemical Instrumentation" feature for the Journal of Chemical Education

John C. Travis

Recording Secretary, Research Advisory Committee, NIST

Gregory C. Turk

Editorial Board, Atomic Spectrometry Updates
Local Organizing Committee, 4th International Symposium on Resonance Ionization Spectroscopy and It's Applications
Section Chairman, FACSS Program Committee
Inorganic Analytical Research Division Seminar Committee

Thomas W. Vetter

ASTM E-03, Chemical Analysis of Metals
ASTM E-03.01, Ferrous
ASTM E-03.91, Editorial
ASTM E-03.92, Standards

Robert L. Watters, Jr.

ASTM E-03, Chemical Analysis of Metals
ASTM E-03.01, Ferrous

Yung-Chi Wu

ASTM D-19 Water

Rolf Zeisler

NIST Reactor Safety Evaluation Committee
Chairman, Trace Element Analysis Committee, Technical Group for Biology and Medicine, American Nuclear Society
CAC Quality Assurance Committee
General Chairman, International Conference on Nuclear Analytical Methods in the Life Sciences
International Committee on Nuclear Analytical Methods in the Life Sciences

4. Other

a. Seminars

October 8, 1987

Dr. Biserka Raspor, Center for Marine Research, Rudjer Boskovic Institute, Zagreb, Yugoslavia, "Cadmium Induced Proteins from Mytilus Galloprovincialia - A Possible Biological Reference Material for Environmental Analysis". (Division Sponsor: W. F. Koch)

October 8, 1987

Dr. Subrahmanyam Gangadaharan, Bhahba Atomic Research Center, Bombay, India, "Potential Applications of Neutron Beams at BARC". (Division Sponsor: R. G. Downing)

October 19, 1987

Dr. Halina Rubinsztein-Dunlop, Department of Physics, Chalmers University of Technology, Gothenburg, Sweden, "Laser Enhanced Ionization Spectrometry in Analytical Flames and Furnaces". (Division Sponsor: J. C. Travis)

November 19, 1987

Ms. Theresa M. Sullivan, Department of Chemistry, University of Maryland, College Park, MD, "Ko Method of Analysis: Data and Results". (Division Sponsor: R. F. Fleming)

November 19, 1987

Dr. Robert L. Kay, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA, "Electroanalytical Research". (Division Sponsor: W. F. Koch)

December 4, 1987

Dr. Richard L. McCreery, Chemistry Department, Ohio State University, Columbus, OH, "Novel Spectroscopic and Electroanalytical Techniques for Trace Analysis: Fiber. Optic Raman Spectroscopy and Double Modulated Electrochemistry". (Division Sponsor: K. W. Pratt)

December 7, 1987

Dr. David M. Coleman, Department of Chemistry, Wayne State University, Detroit, MI, " Segregated Sampling and Excitation". (Division Sponsor: R. L. Watters, Jr.)

January 12, 1988

Dr. Viliam Krivan, University of Ulm, Ulm, West Germany, "High Purity Analysis of Semiconductor Materials". (Division Sponsor: R. G. Downing)

January 22, 1988

Dr. Vincent P. Guinn, Department of Chemistry, University of California, Irvine, CA, "Short-lived Isotopes in NAA: Analysis of Flourine and Use of the Advance Prediction Computer Program". (Division Sponsor: D. A. Becker)

March 8, 1988

Ms. Theresa M. Sullivan, Department of Chemistry, University of Maryland, College Park, MD, "Monitor Neutron Activation Analysis Applied to Superconductor Materials". (Division Sponsor: R. G. Downing)

March 21, 1988

Dr. M. Tezer Esat, Research School of Physical Sciences, Department of Nuclear Physics, Australian National University, Canberra, Australia, "Physico-Chemical Isotope Anomalies: Cr". (Division Sponsor: I. L. Barnes)

March 28, 1988

Dr. Kurt V. Irgolic, Department of Chemistry, Texas A&M University, College Station, TX, "The Speciation of Arsenic Compounds in Biological Tissues". (Division Sponsor: H. M. Kingston)

April 20, 1988

Dr. Muhammad Arif, Research Reactor, University of Missouri at Columbia, Mo, "Analytical Applications of Focused Neutrons". (Division Sponsor: R. G. Downing)

April 22, 1988

Dr. Ira Krull, Chemistry Department, Northeastern University, Boston, MA, "New Analytical Approaches for the Determination and Speciation of Volatile Organomercury and Organotin Species". (Division Sponsor: H. M. Kingston)

April 29, 1988

Dr. Yaoqi Zhou, Department of Chemistry, SUNY at Stony Brook, NY, "pH and Absolute EMF Scale". (Division Sponsor: Y. C. Wu)

June 10, 1988

Dr. Anne P.Thorne, Blackett Laboratory, Imperial College of Science and Technology, London, England, "High Resolution Spectroscopy in the Ultraviolet with a Fourier Transform Spectrometer". (Division Sponsor: R. L. Watters, Jr.)

June 22, 1988

Dr. Helmut Kaiser, Missouri University Research Reactor, Columbia, MO, "Neutron Interferometry and Its Applications and Some Ideas of Focussing a Neutron Beam". (Division Sponsor: R. G. Downing)

June 24, 1988

Professor Harold L. Friedman, Chemistry Department, SUNY at Stony Brook, NY, "New Electrolyte Limiting Law". (Division Sponsor: W. F. Koch)

June 24, 1988

Dr. Franz Lux, Institute for Radiochemistry, Technical University of Munich, Garching, Federal Republic of Germany, "Application of Neutron Activation Analysis in the Development of Anticancer Drugs". (Division Sponsor: R. L. Zeisler)

July 26, 1988

Professor Chai Chifang, Institute of High Energy Physics, Academia Sinica, Beijing, People's Republic of China, "Present Status of Nuclear Activation Analysis in China". (Division Sponsor: R. L. Zeisler)

August 5, 1988

Dr. Jerry D. Messman, Research Chemist, Columbus, Ohio, "Applications of Atomic Spectrometry in a Contract Research Environment." (Division Sponsor: R. L. Watters, Jr.)

b. Conference Sponsored

October 2, 1987

G. Venkatesh Iyengar, International Workshop on Practical Analytical Approaches to the Assessment of Humna Dietary Intake of Nutrients, Toxic Constituents and Radioisotopes, National Bureau of Standards

October 2, 1987

Richard M. Lindstrom, Workshop on Silicon Characterization, National Bureau of Standards.

November 1987

R. Gregory Downing, Workshop on Neutron Depth Profiling for the American Nuclear Society, Los Angeles, CA.

III. Organic Analytical Research Division

Willie E. May, Chief
Michael J. Welch, Deputy Chief

A. Division Overview

The Organic Analytical Research Division conducts research to develop and improve techniques for the preparation, purification, and analysis of organic compounds and uses these techniques in the solution of problems related to national needs. The Division's research is carried out in five groups that are organized along functional lines: (1) **Bioanalytical Techniques**, the activities of which are directed toward development and refinement of methods for the separation and characterization of proteins and other biomolecules, multivariate analysis of two-dimensional electrophoretic protein patterns, and the characterization of reference compounds using nuclear magnetic resonance, polarimetry, and fluorescence; (2), **Analytical Sensors**, the activities of which focus on the development of novel electrochemical methods for the selective and sensitive detection of organic and organometallic species in liquid chromatographic effluents, development of detectors based on thin-film planar waveguide and thermal lensing/deflection approaches, characterization of electrode surfaces modified with polymer-immobilized organometal catalysts, modelling of the transport processes within polymer films and viscous polyelectrolytes, use of immunochemical reactions to provide selectivity for the detection of biomolecules, and development of a generic liposome-based flow injection immunoassay system (3) **Liquid Chromatography**, which involves research focussed on gaining a better understanding of the mechanisms responsible for retention and selectivity in reversed-phase liquid chromatography, development of selective detection systems and multidimensional chromatographic approaches for the analysis of individual compounds in environmental, clinical, and food/nutritional samples; (4) **Gas Chromatography**, which conducts research in high resolution gas and supercritical fluid chromatography, multidimensional gas chromatography, advanced sample preparation techniques (e.g., solid phase and supercritical fluid extraction), and computerized automation of immunochemical reactions to provide selectivity for the detection of biomolecules; and (5) **Mass Spectrometry**, the research of which involves development and use of definitive methods of analysis for clinically important analytes, collision induced dissociation of ions for structure determination, and a variety of mass spectrometric techniques (including thermospray LC/MS) for the quantitation of organic analytes in complex mixtures.

The Division responds to the measurement and standards needs of industry, other government agencies (federal, state, and local), public and private sector institutions and associations, and other research organizations within the National Institute of Standards and Technology. Research efforts in the Division have resulted in the 43 technical articles being published or in press. Division scientists presented 57 talks at technical meetings and conferences during FY88.

During the past year, approximately 50% of our efforts were directed toward research in organic analytical chemistry, another 10% of our research and measurement program provided support to the NIST Standard Reference Materials program, and the remainder of our efforts were in support of other agency programs and to a limited degree, short-term projects performed on a service analysis basis.

A large portion of the Division's support for research (~ 42%) is provided through four "Competence Building" programs. In 1977, the Office of Management and Budget (OMB) recommended, and Congress, approved, $2M for NBS to develop technical competence in various measurement disciplines in support of the core mission and long-range goals. Two of our four Competence programs, "Organic Electrochemistry" and "Protein Stabilization and Characterization" have been ongoing for more than five years and will cease to have Competence funds in FY89. Our program in Organic Mass Spectrometry was evaluated two years ago and will continue this year. Our "Bioanalytical Sensors" Competence Program, is entering it's fourth year. The excellent progress that is being made in this program is described in detail in the Technical Activities and in the Analytical Sensors Group Overview.

The accomplishments made in our Competence and STRS supported research programs will be described in the Group Overviews that follow. There are, however, two major research accomplishments that merit mention here as well. Results from a joint research project conducted in our Liquid Chromatography and Mass Spectrometry Groups demonstrated the potential accuracy and precision of quantitative trace organic measurements using thermospray LC/MS and thermospray LC/MS/MS in conjunction with isotope dilution techniques. We were able to quantify uric acid in our "Human Serum" SRM (909) with an imprecision of ±1% using a simple protein precipitation followed by direct injection of the resulting supernate on a reversed-phase LC column. The results of both the LC/MS and LC/MS/MS experiments agreed with the certified value (81 ppm) to within 1%. Additional details concerning this activity can be found in Technical Activity No. 2. The Gas Chromatography Group has developed a multidimensional GC system that provides resolution never before attained for PCB congeners. This system is based on the on-line coupling of columns that separate PCB's based on volatility and molecular shape respectively. Many of the important congeners coelute on conventional GC columns and have identical mass spectra, thereby eliminating the possibility of definitive determination by mass spectrometry. The multidimensional system provides the capability for unambiguous identification and a means for quantitation of environmentally significant PCB congeners. Further information concerning this research effort can be found in Technical Activity No. 8.

Our longstanding programs with the National Cancer Institute (NCI), National Oceanic and Atmospheric Administration (NOAA), Environmental Protection Agency (EPA) and the Department of Energy (DoE) have continued. A new multi-year program with the Department of Defense (DoD) is being established and an effort with the U.S. Department of Agriculture (USDA) initiated in FY86 has resumed. Specific research efforts in support of these other federal agency programs were: serving as the Quality Assurance Center and Reference Laboratory 1) for a network of NCI grantee laboratories that measure blood levels of vitamins A, C, E, and beta-carotene as part of the process of investigating their efficacy as cancer chemopreventive agents and 2) in a pilot effort to determine the efficacy of the use of two-dimensional electrophoresis with computer image analysis in protein modulation studies of human colon tumor cells; developing SRMs, providing specimen banking support, and serving as the reference laboratory for contractors of the NOAA Oceans Assessment Division involved in the National Status and Trends Monitoring program; providing reference materials and analyses for establishing NIST benchmark values for EPA quality control and proficiency testing samples for EPA EMSL Laboratories at Cincinnati and Las Vegas; establishing a program for the provision of reference materials to support the measurement of DNA-adducts of toxic organic species in body fluids; providing QA services for the Army demilitarization of chemical agents program and development of procedures for the immobilization of biomolecules on nylon and fiber optic supports. Our program with the USDA involves the critical evaluation of the proposed "o-tyrosine method" for performing post-irradiation dosimetry on meats and poultry. Further discussion of many of these activities follow in the Group Overviews and Technical Activities.

We have continued our active support of the NIST Standard Reference Materials (SRM) program. Our direct funding for SRM related activities continues to represent approximately 10% of our budget. However, reference materials related activities and research on matrix stability constitute a much larger portion of our total research and measurement efforts within the Division. Over the past ten years, the number of SRMs certified for organic constituents has increased from ten pure crystalline materials to more than fifty materials that include instrument calibration and performance materials, as well as clinical, environmental and food/nutritional matrices with certified values for trace organic constituents. Nineteen SRMs have been certified during the past two years. Among these SRMs was the first of a series of Drugs of Abuse in Urine SRMs and two Cholesterol in Serum materials. SRM 1507 contains the primary urinary metabolite of marijuana at a concentration of ≈ 20 ng/mL upon reconstitution of the freeze-dried urine matrix. This SRM will provide an accuracy benchmark for the drug monitoring community. SRMs 1951 and 1952 are each comprised of three serum pools with certified levels of total cholesterol. SRM 1951 is being issued as a frozen liquid and SRM 1952 is a freeze-dried serum. These materials will directly assist manufacturers and clinical laboratories in improving the accuracy of cholesterol determinations. Improved accuracy will result in better and more cost-effective health care for the public. Details concerning the Division's other FY88 SRM activities are provided in the Group Overviews and Technical Activities that follow.

The following SRM projects are in progress and should be completed during the coming year: the certification of a Cocaine in Urine SRM in collaboration with the College of American Pathologists; the development of a vitamins in serum SRM in collaboration with NCI; the development of a marine sediment and a marine tissue SRM, each having certified values for selected PAH, pesticides, and PCB congeners in collaboration with NOAA; hexane/isooctane-based calibration solution SRMs for PAH, pesticides, and PCB congeners; development of a Diesel Particulate SRM for Bioassay in collaboration with EPA and the World Health Organization; providing values for selected organic nutrients and clinically significant compounds in a Mixed Diet reference material.

Research efforts in the Division continue to be bolstered by the contributions of a number of Guest Scientists (8), Research Associates (4), and high school, undergraduate and graduate students (5). Their individual contributions to specific programs are described in the Group Overviews and Technical Activity 4.

The overall objective of our research program continues to be directed toward the refinement of existing, and development of new, approaches to performing accurate and precise determinations of both macro and micro quantities of organic constituents in a wide variety of matrices. In that regard, significant progress was achieved in all five of the research thrusts identified for FY88:

(1) to commence the evaluation of the uniformity of immune-response on immune-mediated lysis of liposomes to release marker compounds for a variety of antibody-antigen reactions, and to optimize silanization reaction conditions for the derivatization of glass beads to be used in the immunoreactor column of the associated flow-injection based biosensor devices; (see Analytical Sensors Group overview and the Technical Activity 2)

(2) to develop a liquid chromatography-laser enhanced ionization method for the determination of alkyl tin species in extracts from environmental samples; (see Analytical Sensors Group Overview)

(3) to evaluate the accuracy and precision provided by isotope dilution thermospray LC/MS; (mentioned previously, also see MS Group Overview)

(4) to evaluate the use of supercritical fluid chromatography for the separation of non-chlorinated pesticides; (see GC Group overview and the Technical Activities)

(5) to develop chromatographic and electrophoretic techniques for the separation and quantitation of biomolecules in complex mixtures and for the isolation of milligram quantities of pure proteins. (See Bioanalytical Techniques Group Overview).

Research thrust areas for the coming year are discussed in detail in the Group Overviews that follow. Our most pressing staffing need is a mass spectrometrist with trace organic analytical experience, to fill the void created by the loss of two Ph.D. level staff. We also are interested in attracting a spectroscopist with experience in GC- and LC-FTIR.

1. Bioanalytical Techniques Group: Overview

The activities of the Bioanalytical Techniques Group are directed primarily towards (1) developing means for separating and characterizing proteins, peptides, and other biomolecules to address standards needs in biotechnology, (2) developing nucleic acid standard materials, (3) performing of research in high-field nuclear magnetic resonance spectroscopy, and (4) investigating of the use of immunochemical reactions to provide selectivity for the detection of biomolecules.

Research efforts with proteins and peptides have been focused on improving ultra-sensitive methods for protein separation, visualization, and identification. We have continued to apply our capabilities for protein separation and identification to specific problem areas.

We have become proficient in the use of the Visage imaging system for two-dimensional electrophoresis and have now upgraded our imaging capabilities by the procurement of a CCD camera capable of providing resolution of about 175 micrometers per pixel. Enhanced hardware and software are providing the capability of imaging and processing many more two-dimensional gels per day than was previously possible with the older system.

In work designed to enhance capabilities for NMR analysis of complex biomolecules, a number of new two-dimensional (2D) spectrum editing methods have been explored during the past year. In extension of previous work on two-dimensional POMMIE (POMMIE = Phase Oscillations to MaxiMIze Editing) J(CH)-resolved ^{13}C NMR spectrum editing, we have investigated the feasibility and limitations of 2D POMMIE pulse sequences for the separation of carbon-proton chemical shift correlation ^{13}C NMR spectra into CH, CH_2, and CH_3 subspectra (2D spectrum editing). The purpose of these experiments is to simplify the 2D NMR spectra of complex molecules, thus facilitating spectral interpretation, assignment, and the separation of overlapped peaks. Selected carbohydrate, macrolide antibiotic, and tri- and tetra-peptide derivatives have been used as model compounds in these studies. By this means, very good 2D carbon-proton chemical shift correlated CH and CH_3 subspectra could be obtained, but, for typical carbohydrate and peptide derivatives, the generation of good CH_2 subspectra was more difficult. Based on our results, a number of strategies for refinement of 2D POMMIE spectral editing have been investigated, including consideration of factors involved in both data acquisition and processing. The use of these methods, either alone or in combination, has generally yielded 2D POMMIE subspectra of better quality, for both J(CH)-resolved and carbon-proton shift correlation techniques.

We are continuing to work on developing capabilities for enzyme and other protein immobilization by solid-phase binding with novel binding "spacer-arm" chemistries. We have continued our studies with the Army in evaluating long-term stability of enzymes bound on glass fibers. This work was presented at a meeting in Aberdeen, MD in April 1988, and a paper is now being completed for publication.

We have continued to concentrate some of our efforts on characterizing protein structure. As a probe molecule, we are establishing the three-dimensional structures of the chelated and non-chelated forms of pyoverdine P_{f244}. This fluorescent siderophore, produced by growing Pseudomonas fluorescens 244 in an iron-poor medium, has been isolated and purified (>200 mg total yield) and analyzed for amino acid content using phenylisothiocyanate derivatization and HPLC analysis. Structure determination has started by the completion of baseline one-dimensional NMR experiments on the de-ferrated peptide and on the peptide chelated with gallium. Homo- and heteronuclear two-dimensional NMR techniques also have been initiated. A second objective in this program is to establish the binding site of the siderophore of interest for the tri-butyl tin cation. Two-dimensional proton NMR spectroscopy methods (COSY, SECSY, NOESY) will establish the primary and secondary structures. Heteronuclear NMR analysis of ^{15}N-labeled (produced biosynthetically) and ^{13}C (natural abundance) material will be used to refine PMR-based assignments and to establish the conformational dynamics in molecules.

Research in carbohydrate-protein interactions is proceeding through the detailed examination of the chemical specificity that occurs in the heparin-fibronectin system. This information will help in understanding the role of complex carbohydrate binding to protein sequences and the implication in recognition and control processes within cells and their environment. Such work includes 1) separation of fragments of heparin and fibronectin by HPLC and electrophoresis, 2) structural analysis by NMR and mass spectrometry, and 3) analysis of binding by equilibrium dialysis and spectral perturbation. Studies on the interaction of heparin with fibronectin have been performed in collaboration with K. Ingham and S. Brew at the American Red Cross Biomedical Research and Development Laboratory, Rockville, MD. These studies have characterized the stoichiometry and affinity of heparin binding to fibronectin and the isolated domains of fibronectin. Subsequent studies are aimed at determining the specific sulfate groups on heparin and the specific peptide sequence within the heparin binding domains of fibronectin that are required for this interaction. In addition, thermodynamic studies of heparin interaction with fibronectin have been performed in collaboration with F. Schwarz of the Chemical Thermodynamics Division. Preliminary studies show large changes in the cooperativity of the temperature-induced unfolding transition in fibronectin in the presence and absence of heparin. This indicates that conformational changes in the protein are induced by heparin binding. Further studies are aimed at determining specific interactions of heparin with the isolated domains of fibronectin.

As part of our QA efforts with the National Cancer Institute, serum-based control materials for retinol, α-tocopherol, and beta-carotene have been prepared and tested routinely to study the effects of storage time and temperature. In addition, these sera have been very useful in interlaboratory studies to measure the beneficial effects of value assigned reference materials on the quality of measurements. A graphical reporting procedure has been developed that greatly facilitates interpretation of data.

High performance liquid chromatographic techniques were extended from protein and peptide separations to nucleic acids and high molecular weight DNA fragments. Our diode-array HPLC system has been upgraded by the addition of new software and hardware. We now have the capability of performing amino acid analysis by use of the phenylisothiocyanate derivatization procedure. This enhances the sensitivity and reproducibility of our amino acid studies.

During the past year, a new system for DNA electrophoresis has been obtained and is operating successfully. The unit is based on a technique termed "Transverse Alternating Field Electrophoresis" and allows the separation of DNA up to several million base pairs. We have separated yeast chromosomal materials and are using the system to monitor the size and quality of DNA to which various adducts will be attached. These materials are being prepared for contract laboratories of the Department of Energy.

We have also successfully set up and operated a system for preparative isoelectric focusing. Using the technique, we are preparing purified fractions of selected proteins for use as two-dimensional electrophoretic markers. This work was necessary because none of the protein markers currently available from commercial sources are sufficiently pure for standards work.

For the upcoming three years, planning details for the various programs in the Bioanalytical Techniques Group include:

(1) Separating and characterizing proteins, peptides, and other biomolecules; a) investigate analytical methods which are able to detect proteins and peptides at the sub-nanogram level: develop mass spectrometric methods for probing peptide structure; improve techniques for neutron activation of metal-binding proteins; b) provide standards to the research community

that utilizes separation methods for analytical studies of proteins and peptides; c) continue research on interactions of selected proteins with chemically modified supports: continue with hydrophilic supports and extend to mixed-bed supports; selectively immobilize enzymes on hydrophilic beads and other supports to improve stability; improve silver staining procedures by understanding interactions of metals with proteins; investigate "spacer-arm" binding to selected polymeric materials; d) develop database capabilities with imaging of two-dimensional electrophoresis; e) study the interactions of immobilized proteins on surfaces through use of Diffuse Reflectance Infrared Detection; and f) develop capabilities in Capillary Zone Electrophoresis.

(2) High-field NMR Spectroscopy: a) develop optimal pulse sequences for NMR studies of peptide structures; b) continue to develop expertise in structural studies of biomolecules.

(3) Protein stabilization: a) immobilize enzymes and antibodies for specific applications in biosensor methodology.

(4) DNA Adducts: develop materials to be used in a quality assurance program for the Department of Energy and as potential reference materials.

This coming year we will be joined by an NRC post-doctoral researcher, Ms. Edith Grabbe, who is completing her Ph.D. work at the University of North Carolina and will be joining us at the end of the year. Her proposed work will be focused on mechanisms of enzyme and protein immobilization to surfaces.

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2. Analytical Sensors Group: Overview

While this Group has historically focused on electroanalytical methods, optical methods have taken on a more significant role in our activities. The principal areas of ongoing research include: 1) development of novel methods for selective/sensitive electrochemical detection in liquid chromatography, 2) characterization of electrode surfaces modified with polymer-immobilized organometal catalysts, 3) modeling of transport processes within polymer films and viscous polyelectrolytes, 4) silanization and derivatization of glass surfaces for planar waveguide and immunoreactor applications, 5) development of liposome-based flow injection immunoanalysis systems, and 6) investigation of novel optical detectors based on thin-film planar waveguide and thermal lensing/deflection approaches. The common goal of this work is to increase the sensitivity and selectivity of electrochemical and optical measurements for trace organic analysis. The research tools we are using to achieve this goal include: square-wave, differential-pulse, rotating ring-disk, and cyclic voltammetry; chronoamperometry and chronocoulometry; frequency-dependent and steady-state fluorescence and internal reflectance spectroscopy; hybrid techniques such as spectroelectrochemistry and liquid chromatography with uv/visible and electrochemical detection.

We have continued to make good progress on the research goals targeted in the Organic Electrochemistry and Bioanalytical Sensors Competence Building Programs. Polymer-modified electrodes have been developed and are undergoing evaluation. Chemical and electrochemical characterization of cobalt-containing "capped" metalloporphyrins for use as electrocatalytic sensors is nearing completion and a paper on this work is in preparation. Also, a new type of porphyrin polymer-modified electrode has been prepared which shows excellent coating characteristics (uniformity and stability), a high degree of electroactivity, and selective permeability. This process, which is described in a recent paper in J. Electroanal. Chem., involves the production of a tetra-quaternized porphyrin which can hydrolyze to form the desired polymeric film. Another polymer modification process under investigation involves the thermal polymerization of the copolymer formed between bismaleimide and diene-containing ruthenium complexes and deposition on glassy carbon electrodes. These polymer films displayed stable redox behavior and facile electron transfer between the ruthenium (II/III) redox centers and the carbon electrode in a variety of solvents at ambient and elevated temperatures. As part of our efforts to understand and model the kinetics and transport processes in polymer films, we have investigated the electrochemical behavior of ferrocene in polyethylene oxide (PEO-400), a solid/viscous liquid solvent. Using a variety of electrochemical techniques, the redox behavior of ferrocene was studied at various temperatures. In spite of large resistive effects, we were able to compare the experimental results with simulated results and obtain heterogeneous electron-transfer rate constants for this quasi-reversible system. In addition, large-step chronoamperometry, while not showing simple Cottrell behavior, provided data for the calculation of estimated diffusion coefficients. A paper on this work has been submitted for publication, as well as another paper on the application of discontinuous integrals in chronoamperometry using planar disk electrodes.

The goal of the Bioanalytical Sensors competence building project is to use the specificity of immunological recognition coupled to chemical and/or biochemical amplification to provide highly selective and sensitive measurement of organic analytes. While we do not expect the present design of our system to have increased sensitivity over current immunoassays, we do expect significant improvements in convenience, reproducibility, and accuracy. The first step toward this goal, the encapsulation of electrochemical or fluorescent markers, or biocatalysts (enzymes), in the aqueous volume of a liposome has been successfully achieved. Amplification of a competitive immunological binding event may then be achieved by the lysis of the liposome, thereby releasing thousands of marker molecules for detection or enzyme molecules for subsequent reaction and product detection (double amplification). We have been approaching this objective from two parallel directions; a homogeneous immunoassay and a heterogeneous flow injection immunoassay.

The development of a homogeneous immunoassay, based on the preconcentration and measurement of liposome-released ferrocyanide by a dual-function polymer modified electrode, has been completed, and a paper describing the characterization of the ferrocyanide-loaded liposomes and preliminary investigations of the electrode behavior has been published in Anal. Chem. The physical parameters and stability of the ferrocyanide-loaded liposomes were studied by electrochemical and spectroscopic methods. Studies were performed in which the marker ions were released from within the liposome by surfactant or complement lysis. In the classical complement pathway, an antigen/antibody-specific reaction occurs when an antigen-sensitized liposome immuno-specifically binds with the corresponding antibody in the presence of complement. Complement is activated and forms a membrane attack complex which results in the lysis of the liposome and release of the encapsulated ferrocyanide which is then detected by differential pulse voltammetry. To further increase the sensitivity of the method and to prevent fouling of the electrode surface by serum proteins and membrane lipids, a special dual-function anion-exchange polymer modified electrode was developed. Studies with this modified electrode have demonstrated the ability of the anion-exchange polymer to preconcentrate the ferrocyanide at the electrode surface as well as to protect the electrode from fouling. A paper describing the homogeneous immunoassay for the model analyte, anti-dinitrophenol IgM, is in preparation.

The flow injection immunoanalysis (FIIA) system under development is discussed in Technical Activity No. 4 and is based on an immunochemical reaction taking place in a packed-bead column in which the antibody fragments (Fab') are covalently bound to small, nonporous-glass beads. Competitive binding occurs in this column when a solution of the antigen-derivatized, marker-containing liposome is mixed in the flow injection system with the antigen sample solution and flowed through the reactor column. Unbound liposomes are carried downstream for non-selective detergent lysis to release the marker molecules which then pass into the detector for quantitation. This flow injection scheme is but one of many that can be used to provide the desired immunoassay.

The purpose of developing this FIIA approach is to provide a fully automated immunoassay system which can be regenerated for sequential analysis and calibration. At the present time, several of the critical elements needed to complete this flow injection immunoassay system have been achieved and the remaining components are nearing completion. The stability of the liposomes, both in storage and under flow conditions, has been successfully demonstrated. Their hydrodynamic behavior, which is unique compared to molecular and particulate species under flow injection conditions, has been carefully characterized, and a paper on these results has been published in Anal. Chem. Silanization of the glass beads has been a particularly difficult problem which now seems to be on the verge of solution. As part of this study, we have developed sensitive ^{14}C and fluorescent assays for the quantitation of the degree of silanization of the bead surface. We are now also studying ways to immobilize antibodies so that their activity is preserved, as well as ways to gently dissociate the antigen-antibody complexes to regenerate the binding activity of the immobilized antibodies. Finally, we have developed a novel generic approach to liposome derivatization which involves the use of a biotinyl-phosphatidylethanolamine as a component of the liposome membrane. Biotinylated analyte analog is then linked to the biotinylated liposomes using avidin, a multivalent biotin-binding protein. A paper on this work has been submitted to Biochim. Biophys. Acta.

Research is continuing to extend this flow injection immunoassay one step further in sensitivity. Instead of loading the liposomes with electroactive or fluorescent markers, an enzyme (horseradish peroxidase) will be encapsulated and subsequently released in the presence of its peroxide substrate and p-fluorophenol which reacts enzymatically to produce fluoride ion which will be detected by a fluoride ion-selective electrode. This approach will provide a double amplification of the immunoreaction; one being the release of the encapsulated enzyme and the other being the enzymatic production of fluoride product. After some serious problems with electrode fouling, which were overcome by introducing a special wash channel containing Triton X-100 to the FIA system, most of the components of this scheme have been shown to function independently, and testing is now in progress to optimize their performance in the flow injection mode of operation.

At the recommendation of last year's Panel, we have chosen a more relevant analyte than our original model compound, dinitrophenol, for development and testing of this FIIA system. Our current prototype uses anti-theophylline antibody for the determination of the therapeutic drug, theophylline. It is estimated that over 100,000 clinical assays are performed annually for this clinically important analyte. Since we have no facilities for producing antibodies, one of the most important considerations in choosing an antigen-antibody system for prototype development was the availability, in research quantities, of an antibody of reasonable affinity. Because of the generic nature of the antibody immobilization and liposome derivatization procedures, once the prototype system is completed and characterized it should be easily adaptable to a wide variety of analytes. We have been encouraged in the importance and relevance of this work by the interest the FIIA system has received for commercial development. A patent application on this system was filed in June. In addition, we anticipate that our work on antibody immobilization will aid in the development of other techniques such as large-scale purification of biotechnology products (including affinity HPLC), extracorporeal detoxification, and fiber-optic sensor applications. In our research, we are addressing very important quantitative aspects such as the maintenance of binding activity after immobilization, the ability to regenerate immobilized antibody activity for reuse, and long-term stability; all of which are problem areas which are currently limiting the development of these technologies.

Work has been initiated towards developing absorption- and fluorescence-based optical sensors for immunoassay methods using planar thin-film dielectric waveguides. These waveguides have been fabricated from silicon nitride using low-pressure chemical-vapor deposition. While these devices are currently undergoing evaluation, the initial results are promising as the Si_3N_4 waveguides are more durable, easier to derivatize, and offer a wider range of optical properties than similar waveguides fabricated from polymeric materials. The detection system for the fluorimetric sensor, an optical-fiber bundle coupled to a polychromator with an optical multichannel analyzer detector, has been assembled. Work remaining on the planar waveguide sensors involves improving their performance at blue wavelengths, covalently derivatizing the waveguides, and incorporating the derivatized sensor into an FIA system.

Concomitantly, we are developing thermo-optical methods of detection using the thermal lens phenomenon as an optical detector for the FIIA project. Currently, a two-laser, pump/probe system is being evaluated as a suitable geometry for FIIA. Sensitivity approaching that of fluorescence methods is expected while reducing the system complexity. In addition, experiments are underway to determine the feasibility of using semiconductor lasers for these measurements. The expected advantages would be lower cost, increased durability, and miniaturization of the optical layout.

Liquid chromatography with electrochemical and optical detection has continued to prove its usefulness in a variety of programmatic applications. As part of the continuing NCI Cancer Chemoprevention Program, work is in progress to develop and apply an LC/UV method for the determination of the drug 4-hydroxyphenylretinamide and its major metabolite in serum. A new method for the determination of organic thiols in marine sediments was developed using LC(oxidative)EC detection at a gold/mercury thin-film electrode. The separation of these hydrophilic compounds was enhanced using trihaloacetic ion-pairing buffers. One paper on organic thiol detection was published in Anal. Chem.; another on the separation chemistry of organic thiols has been accepted for publication in J. Chromatog.; and a third paper on modeling interrelationships of organic thiols and trace metal concentrations in marine sediments is in preparation. Work is in progress on the pulsed LCEC detection of thiols and disulfides. In collaboration with G. Turk of the Inorganic Analytical Research Division, organotin cations have been determined in marine sediments by LC/LEI (laser enhanced ionization). Suitable separation and detection conditions were devised, and a method was developed for the extraction of the tributyltin compounds from the sediments. A paper on this technique has been accepted for publication in Anal. Chem. In addition to the LEI detection of the tributyltins, studies have been initiated on the laser activation and modification of glassy carbon electrodes for two applications: 1) selective activation of small areas of a polymer-deactivated electrode surfaces to make microarrays (currently using photopolymerized allyl sulfide to form the inert polymer film on the electrode and a focussed laser beam to vaporize selected micrometer-sized areas of the polymer film) and 2) application of laser activated electrodes to the determination of organic analytes.

In the coming year, we plan to continue our efforts in the ongoing projects discussed above as well as expand into the new areas of microarray-electrode and thermal-lensing/deflection detectors for application in HPLC, SFC, and FIA. In addition, we plan to test, evaluate, and optimize the FIIA system and compare its performance to existing immunoassay techniques.

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3. Gas Chromatography Group: Overview

The Gas Chromatography Group conducts research in the areas of high resolution gas, multidimensional and supercritical fluid chromatography, advanced sample preparation techniques and micro-computer applications. To maintain state-of-the-art trace organic analytical competence, which is used to certify complex Standard Reference Materials (SRMs), address the measurement and quality assurance needs of other Federal and State agencies, and disseminate technical information.

Our efforts in capillary supercritical fluid chromatography (SFC) have been greatly accelerated with the arrival of Dr. Albrecht Munder, an Alexander Humboldt Fellow from the University of Ulm in West Germany. Because of his efforts, we now have an empirical understanding of the SFC experiment and have the capability to arrive at initial conditions for most analyses. Dr. Munder has also obtained the precision and accuracy levels for which our instrument was designed. He has obtained enough data to start initial physicochemical modeling of the SFC separation process. We have developed a series-coupled dual-detection apparatus which allows both UV and FID detection without effluent splitting. While most of our work has been on nitro-group containing compounds, we have shown that SFC is amenable to the separation of large PAH isomer (MW >302) non-chlorinated pesticides, and vitamins.

We have used our multidimensional gas chromatographic system for the analysis of extremely complex chemical mixtures. During this past year, we have shown the feasibility of using this technique for the congener-specific determination of polychlorinated biphenyls and will shortly use it for certification of SRM 1939-40 (polychlorinated biphenyls on terrestrial soil).

We are constantly improving our abilities in sample preparation for chromatographic analysis. We are using a number of HPLC techniques to cleanly remove analytes from difficult matrices such as tissue, contaminated sediment and biological fluids. While we continue to very successfully use conventional methods such as Soxhlet extraction, normal phase and size exclusion chromatography, we are also investigating some novel techniques, such as the use of on-column chemical modification of congeneric mixtures for class determinations and supercritical fluid extraction of matrix samples.

The controlling CPU of the laboratory information management system (LIMS) that the GC Group developed and used for the past three years, has been replaced by an IBM series PS/2 model 80 CPU. This microprocessor not only supports all existing MS/DOS software, such as LOTUS 123, Wordperfect, etc., but has the required speed, memory capacity and disk storage to handle the amount of data acquired by the Group. This year, novel LIMS software has been written to allow user manipulation and recalculation of chromatographic data. These programs are window oriented for ease of operation and provide a tremendous amount of versatility. Also, to improve the stability of stored data, we now store raw chromatographic data on optical disks instead of the more volatile magnetic diskettes.

As in past years, the Group has spent a great deal of effort contributing to the solution of Other Agency measurement problems. Our quality assurance program for the National Oceanic and Atmospheric Administration's (NOAA), National Status and Trends Program has continued to expand in scope. We have formulated and completed certification measurements on two new calibration solution Standard Reference Materials (SRMs) to complement those certified in FY87. These SRMs, 2261 and 2262, are comprised of 15 chlorinated pesticides and 28 polychlorinated biphenyl congeners, respectively, and are at a concentration approximately ten times greater, 3 μg/g, than the similar solution SRMs produced in FY87. A sediment material (SRM 1941) and a tissue homogenate material (SRM 1974) are also in progress. Certification measurements for polycyclic aromatic hydrocarbons have been completed and information values for selected pesticides and polychlorinated biphenyl congeners have been generated for the sediment material. We are presently finishing the homogenization step for a tissue homogenate material and hope to begin certification early in FY89. This SRM consists of cryogenically homogenized mussel tissue and will be certified for selected polycyclic aromatic hydrocarbons with information values for selected chlorinated constituents. We have also conducted three intercomparison exercises both using gravimetrically prepared solutions of analytes and a cryogenically homogenized tissue material. Results of the solution intercomparison exercises have indicated that most of the participating laboratories are outside of the desired performance criteria set by NOAA. FY89 NIST/NOAA QA milestones will address this shortcoming by conducting additional intercalibration exercises with similar solution materials and other methods such as training courses and on-site guidance on laboratory procedures.

We have analyzed a number of sediment and tissue samples as part of a specimen banking component of our Reference Laboratory function for NOAA's Mussel Watch and Benthic Surveillance Program. We are using high resolution, 60-meter capillary columns in conjunction with an improved HPLC sample clean-up procedure, developed in FY87. The visual quality of the resulting chromatograms and the analytical precision of the data have improved significantly.

A number of additional human liver samples, from the National Biomonitoring Specimen Bank were analyzed for pesticides and PCB congeners using a modified sample preparation procedure. Two sets of Quality Assurance Materials from EPA/Cincinnati were analyzed as part of the process of establishing NIST traceability. A twenty-eight component concentrated (3 µg/g) PCB congener calibration solution was prepared, analyzed and delivered to EPA/Cincinnati for use as a multipoint calibration standard for EPA Standard Method 624 (PCB congeners by GC/MS). A volatile organics in human whole blood reference material, requested by EPA/Las Vegas, has been prepared, measured, and delivered.

We have initiated a new program sponsored by the Department of Defense. Under this program, NIST will develop reference methods for the analysis of surety materials based upon the use of internal standards. We will also establish relative response factors to be used with the methods so that DoD contractors will not require authentic standards to perform analyses. Development of these "reference" methods will involve the evaluation and selection of appropriate internal standards for each surety agent. Most of the effort this year has been in the modification of the Toxic Handling Laboratory so that the toxic surety materials can be used in a safe and secure environment. We have, however, identified over 15 possible internal standards for use with the surety agents.

The Group has made a significant contribution to the Division's SRM program. In addition to the NOAA supported activities, we have commenced certification measurements of two terrestrial soils (SRM 1939-40) containing high concentrations (µg/g) of polychlorinated biphenyls. Additionally, we have developed and improved a protocol for the determination of the purity of chemical materials used in the SRM program. This protocol employs both chromatographic and calorimetric data for the purity determination. We have obtained a differential scanning calorimeter and are using this instrument to confirm the gas chromatographic purity measurements of 68 compounds used to make up calibration SRMs. This year, using this protocol, we have confirmed the purity of over 75 lots of chemicals.

While the Group is heavily committed to its Other Agency and SRM work, we realize the need to concurrently pursue an active research program to maintain our cutting-edge measurement capabilities. We hope in the next three years to make substantial progress in four areas. First, we want to continue to develop our expertise in multi-dimensional gas chromatography and utilize this technique to make both trace organic analytical and purity measurements. We desire to delve further into the retention mechanisms of capillary supercritical fluid chromatography and are hopeful that we will be able to maintain the momentum given to us by Dr. Munder. We will also investigate the use of the new capillary column technological breakthroughs such as ultra-thin films and high temperature phase coated columns. We hope to use these state-of-the-art columns for high resolution separation of biomolecules of interest to other Groups within the Division. Finally, we want to continue to carry on research in sample preparation methodology and on-column chemical modification of congeneric and isomeric analytes for accurate total class quantitative determination.

If we are to maintain our current level of research activity and also fulfill our Other Agency commitments, we will need a permanent staff member to replace Dr. Munder at the end of his postdoctoral appointment. We plan to expand our measurement capabilities to include a capillary compatible FTIR GC detector which will allow nanogram level isomer-specific detection of congeneric classes of compounds such as PAC, chlorinated naphthalenes and biphenyls, volatile nutrients and polar non-chlorinated pesticides. Such an instrument can be series coupled with the MSD, to remove an additional degree of freedom for molecules to escape detection and identification. This detector, with some modification, also be compatible with our capillary SFC instrumentation.

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4. Liquid Chromatography: Overview

The activities of the Liquid Chromatography Group continue to be focussed on gaining a better understanding of the mechanisms responsible for retention and selectivity in liquid chromatography (LC), and applying this information to the development and improvement of methods for the isolation, separation, identification, and quantitation of individual components in various matrices.

Physical and chromatographic characterization of alkyl-bonded phases continues to be a major area of research in the understanding of reversed-phase LC retention mechanisms. An investigation of the relationship between the alkyl-bonded phase thickness and the selectivity (i.e., relative separation) for isomeric compounds is described in Technical Activity No. 1 and has been published in **Analytical Chemistry 59**:2309-2313 (1987). For a series of alkyl-bonded phases with chain lengths ranging from C_8 to C_{30}, selectivity for polycyclic aromatic hydrocarbons (PAH) increased with increasing phase thickness. In several of our studies, we have used a mixture of three PAH to characterize the selectivity of reversed-phase LC stationary phases. This mixture contains benzo[a]pyrene (a planar solute) and phenanthro[3,4-c]phenanthrene and tetrabenzonaphthalene (nonplanar solutes). The differences in elution order of these three components are useful in classifying C_{18} stationary phases (e.g., monomeric or polymeric synthesis) and predicting their ability to separate more complex mixtures of PAH isomers. This mixture was used recently to evaluate the selectivity of over 25 commercial C_{18} columns and as a result, we have proposed a stationary phase classification system based on this test mixture (**J. High Resolut. Chromatogr. Commun. 11**:383-387 [1988]). This mixture has been distributed to a number of LC researchers to determine its potential as a LC column performance SRM.

Polymeric C_{18} phases exhibit shape selectivity for the separation of isomeric PAH that is similar to the shape selectivity observed for liquid crystalline phases in gas chromatography (GC). Relative retention measurements for several sets of isomeric PAH on a polymeric C_{18} phase (reversed-phase LC) and liquid-crystalline polysiloxane stationary phase (capillary GC) were compared and correlated with the simple length-to-breadth shape descriptor of the solute. Similar retention behavior was observed for both chromatographic systems. In fact, anomalies in elution order relative to length-to-breadth ratios were generally found to be consistent in both chromatographic systems and could often be ascribed to secondary shape factors such as the planarity of the molecule. The similarity in selectivity for reversed-phase LC and liquid-crystalline GC should extend beyond PAH (and other polycyclic aromatic compounds) suggesting that excellent separations of other isomeric compounds that are resolved on liquid-crystalline phases in GC may be achieved by reversed-phase LC on polymeric C_{18} phases. The results of this study have been published in **Chromatographia 25**:473-479 (1988). Investigations in progress indicate that the temperature of the column greatly influences the monomeric-like or polymeric-like behavior of the stationary phase. One goal of all of the above studies involving characterization of stationary phases is to gain a better understanding of the exact nature of polymeric vs. monomeric alkyl phases and the mechanisms responsible for separations in reversed-phase LC.

A major new measurement-oriented research effort initiated during the past year involves the evaluation of the quantitative capabilities of thermospray liquid chromatography-mass spectrometry (LC-MS). Our initial approach to evaluate quantitative LC-MS, in collaboration with the Mass Spectrometry Group, has focussed on the use of isotope labeled internal standards to quantify uric acid in SRM 909. These results are described in Technical Activity No. 2 and indicate that LC-MS can provide an additional analytical technique for accurate trace organic analysis in complex matrices.

The LC Group is heavily involved in the application of LC to the determination of trace-level analytes in a variety of sample matrices as part of the SRM program and in support of other agency projects sponsored by the National Cancer Institute (NCI), Environmental Protection Agency (EPA), National Oceanic and Atmospheric Administration (NOAA), and the American Petroleum Institute (API). Four SRMs were completed and issued during the past year for which LC was one of the analytical techniques used for the certification measurements: (1) SRM 1597, Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar; (2) SRM 1563, Cholesterol and Fat-Soluble Vitamins in Coconut Oil (Fortified and Natural); (3) SRM 1647a, Priority Pollutant Polycyclic Aromatic Hydrocarbons in Acetonitrile; and (4) SRM 1507, 11-nor-delta-9-tetrahydrocannabinol(THC)-9-carboxylic acid in Freeze-Dried Urine. The certification of SRM 1597, Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar, is described in Technical Activity No. 19 and the analytical methods for the certification measurements have been published in **Analytical Chemistry 60**:887-894 (1988). SRM 1563, Cholesterol and Fat-Soluble Vitamins in Coconut Oil, is the first food-related SRM specifically prepared for the determination of organic nutrients. SRM 1507, THC in Freeze-Dried Urine, is the first in a series of SRMs for use in the determination of drugs of abuse in urine (see Technical Activity No. 21). The LC methods used in the certification of the coconut oil SRM have been published in **Analytical Chemistry** and methods for certification of the THC in Urine SRM have been submitted for publication.

The LC Group has contributed to the development of five SRMs and a RM that are in the process of certification: (1) NBS/EPA Reference Material 8444, Cotinine in Freeze-Dried Urine; (2) SRM 1588, Organics in Cod Liver Oil; (3) SRM 1941, Organics in Marine Sediment; (4) SRM 1974, Organics in Mussel Tissue (Mytilus edulis), (5) SRM 1508, Cocaine in Freeze-Dried Urine; and (6) SRM 916a, Bilirubin. The cotinine in urine reference material consists of three urine samples that mimic the cotinine urinary levels representative of: (1) nonsmokers with no exposure to cigarette smoke, (2) nonsmokers with passive exposure to cigarette smoke, and (3) smokers. SRM 1588, Organics in Cod Liver Oil, is intended primarily for use in the determination of chlorinated pollutants. However, cod liver oil also contains a relatively high level of α-tocopherol (vitamin E) and is representative of an edible oil. Therefore, two LC procedures were used to obtain data for the certification of α-tocopherol in this SRM. A marine sediment (SRM 1941) and a mussel tissue (SRM 1974) have been collected and prepared for certification as SRMs for use in the measurement of marine contaminants (see Technical Activity No. 18). Certification measurements on the sediment material have been completed using LC with wavelength-programmed fluorescence detection as one of the analytical techniques. Similar LC methodology will be used for the certification of the mussel tissue which has been prepared using cryogenic homogenization to provide a homogeneous frozen powder as the SRM. Measurements of cocaine and cocaine metabolites in SRM 1508 by LC are currently in progress to certify the second SRM for the determination of drugs of abuse (see Technical Activity No. 21). LC measurements were performed on SRM 916a, Bilirubin, to determine the homogeneity of the isomer content and the relative amounts of the three isomers (IIIα, IXα, and XIIIα) which will be provided as information values on the certificate of analysis. During the coming year, the LC Group will be involved in the development and certification of SRMs for fat-soluble vitamins in human serum and total human diet, pollutants in marine tissue, and additional drugs of abuse in urine.

A major effort within the LC group continues to be analytical support for the National Cancer Institute's Micronutrients Measurement Program. This project is described in detail in Technical Activity 13. As the quality assurance laboratory for this program, NIST regularly supplies human serum samples to NCI-supported laboratories for the determination of ascorbic acid, retinol, α-tocopherol, and α-carotene. LC analyses are performed to determine the NIST "reference values" for these samples.The separation of β-carotene isomers is an illustration of the application of knowledge gained from our fundamental investigations of selectivity in reversed-phase LC to achieve challenging separations. Based on our previous studies of the factors that affect LC selectivity for the separation of PAH, we investigated the influence of stationary phase type and synthesis on the separation of β-carotene isomers. As in previous studies with PAH isomers, we found that a polymeric C_{18} phase (trifunctional silane synthesis) provided greater selectivity for the separation of the β-carotene isomers than the monomeric C_{18} phase (monofunctional silane synthesis). Increasing the alkyl chain length or increasing the surface coverage of the stationary phase altered the column selectivity. Polymeric alkyl bonded phases with chain length greater than C_{14} separate trans-β-carotene and the various cis isomers, whereas the monomeric phases would not resolve these isomers. Based on these investigations, we are preparing "tailored" stationary phases to optimize the separation of these isomers. It also appears that the shape and planarity of the carotenoid isomers can be used to predict the order of elution. These studies have allowed us to characterize various β-carotene preparations used in NCI intervention studies to determine the purity and distribution of cis- and trans-β-carotene isomers. By knowing the distribution of these various β-carotene isomers in these preparations, NCI can use formulations that contain only the active (more potent) isomer in their intervention studies. Investigations are continuing to better understand the mechanism of separation of these carotenoids in reversed-phase LC.

Members of the LC Group are involved in another continuing, long-term activity known as the National Biomonitoring Specimen Bank. This program, which is a joint effort with the Inorganic Analytical Research Division, consists of the collection, processing, long-term storage, and analysis of a variety of environmental and biological specimens. These specimen banking activities are supported by several different agencies including EPA, NOAA, and NCI. The expanding scope of the NIST specimen banking activities is described in the Technical Activities.

The LC Group has also been involved in several additional other agency projects such as the determination of herbicides in EPA QA materials (as part of the process of providing NIST traceability), the determination of PAH in marine sediments and tissues (NOAA), the identification of organic markers for residential wood combustion (EPA) (see Technical Activity No. 9), and the development of procedures to isolate benzene from breath samples for subsequent carbon isotopic measurements (API). In research related to the investigation of chemical markers as a means of radiation dosimetry, we have used LC in the isolation and identification of thymine-tyrosine crosslinks, which may serve as such markers (see Technical Activity No. 3).

During the past year, we added one permanent staff member to the LC Group, Dr. Bruce A. Benner. Dr. Benner has worked part-time in the LC Group for the past four years while working on his Ph.D. at the University of Maryland. He has experience in LC, GC, and GC-MS with particular emphasis on environmental sampling and analyses. Märit Olsson, a guest scientist on leave from Kabi Vitrum, a pharmaceutical company in Stockholm, Sweden, has joined the LC Group for one year. Ms. Olsson is using her background in pharmaceutical chemistry to assist us in expanding our investigations of LC column selectivity to include additional classes of compounds (e.g., tetracyclines). Apryll Stalcup, a graduate co-op from Georgetown University, completed her Ph.D and accepted a postdoctoral appointment at the University of Missouri at Rolla.

During the next several years, research in the understanding of LC retention mechanisms will continue to focus on (1) methods for physical and chromatographic characterization of stationary phases, (2) factors affecting selectivity, and (3) comparison of LC and supercritical fluid chromatography (SFC) retention mechanisms. We will continue to develop LC methods for the determination of trace organic constituents in various matrices. For environmental samples, we will continue to improve LC methods for the isolation and determination of the compounds of interest. In the past year, we have focussed a great deal of attention on the measurement of vitamins in serum and food matrices and drugs of abuse and cotinine in urine. We expect that this trend will continue in the upcoming years. In addition to analytical separations, LC has been used more extensively for isolating the analytes of interest from the serum or urine matrices (i.e., sample cleanup) prior to quantitation by other techniques. There is currently a great deal of interest within the liquid chromatography community in the use of micro columns, i.e., microbore and packed capillary LC. We will investigate the applicability of such systems to our measurement problems. To expand our separations capabilities and expertise, we intend to actively recruit graduate students, postdoctoral research associates, and guest scientists with expertise in supercritical fluid chromatography, capillary zone electrophoresis, micro column (microbore or capillary) LC, retention mechanisms, and/or stationary phase characterization.

Stephen A. Wise, Group Leader; Bruce A. Benner, Jeanice M. Brown-Thomas, Richard G. Christensen, Neal E. Craft, Barbara J. Koster, Sam A. Margolis, Märit Olsson, Lane C. Sander, and Xin Zhang.

5. Mass Spectrometry Group: Overview

The Mass Spectrometry Group conducts research in a number of areas which include both basic and applied efforts. The major part of our work continues to be the development of mass spectrometric methods for the accurate quantitation of individual organic compounds in complex matrices. In addition, there is work on the characterization of pure materials for the reissue of Standard Reference Materials (SRMs), and there are continuing efforts to acquire expertise in techniques new to us, such as thermospray and collision induced dissociation, and to gain further understanding of the mechanisms involved in negative ion chemical ionization.

The College of American Pathologists (CAP) Reference Laboratory, established at NIST last year, is fully operational with two full-time Research Associates. About half of the effort is devoted to the continued development of definitive methods and their use to certify NIST SRMs and to assigning values for CAP survey sera and reference materials. This work and related efforts on human serum based SRMs are described below and in the Technical Activities. Work is also in progress on an SRM for cocaine and its metabolites in urine. These cooperative ventures are progressing well: the nature of the materials required has been defined jointly by CAP and NIST; the materials have been procured by the CAP, thus providing economies of scale; the characterization has been done at NIST by the joint efforts of the CAP Research Associates and NIST personnel; and the resulting reference materials may be obtained from either organization. In the other part of our program with the CAP, reference methods have been set up at NIST by a CAP Research Associate and applied to CAP materials. These have included colorimetric methods for calcium, chloride, ethyl alcohol in water, and glucose. The last method required considerable refinement in order to produce satisfactory precision, 0.5%, on more than very small numbers of samples. An additional significant effort has been devoted to the testing of cyanmethemoglobin standards by the accepted reference method, and to serving as a referee laboratory for the International Committee for Standardization in Haematology (ICSH) international cyanmethemoglobin standards. Developing competence in these methods provides NIST with expertise not otherwise available and the CAP with ready access to NIST analytical capability.

The isotope dilution GC/MS definitive methods developed for the quantitative determination of constituents in human serum have been applied extensively. Cholesterol, uric acid, and glucose were measured again this year in SRM 909, Human Serum. The uric acid concentration has shown no statistically significant change over the eight-year lifetime of the material. Glucose continued the previously observed decline at a rate of about 0.7% per year, and, for the first time, a rate of decline for cholesterol, just under 0.2% per year, was established. The certification of two new human serum based SRMs for cholesterol is described in the

Technical Activities. Measurements were also completed on several survey and reference materials for the CAP. These SRMs, reference materials, and survey materials together provide one of the essential elements necessary for reliable and accurate clinical chemistry measurements.

The definitive methods developed for analytes in matrices of clinical interest have much broader potential applications. Examples of this are the adaptations of the method for cholesterol to three different food-related materials which are described in the Technical Activities.

Two new techniques, thermospray for LC/MS and collision induced dissociation, became available to us this year with the acquisition of a triple quadrupole mass spectrometer. The use of these techniques for quantitation, particularly for materials not easily amenable to GC and present in complex matrices, is very promising. The results, achieved in cooperation with the Liquid Chromatography Group, of applying these techniques to the determination of uric acid in serum as a trial material are described in the Technical Activities.

A project for the Department of the Army requiring the development and validation of a method for the determination of 3-quinuclidinyl benzilate (BZ), a chemical agent scheduled for demilitarization, and two of its metabolites in urine was completed a year ago. A new related project has begun. Pure materials and solutions, which will serve as standards for control of the analytical chemistry required for the demilitarization process, will be produced and delivered over a two-year period.

Certification of the first, in an anticipated series, reference material for drugs of abuse has been completed and is described in Technical Activity 21. This SRM (1507) contains 11-nor-delta-9-tetrahydrocannabinol-9-carboxylic acid, the primary urinary metabolite of the active component of marijuana, in lyophilized urine. Stability surveillance measurements are in progress on this material. The isotope dilution GC/MS method developed will also be used to assign values to a similar CAP reference material.

Replacements for two pure material SRMs, Creatinine (SRM 914), and Cholesterol (SRM 911a), have been certified, and the measurements necessary for the certification of a new Bilirubin material are in progress. The determination of the purity of very pure materials and the assignment of uncertainties remains an analytical challenge. Extensive use was made in these efforts of the wide range of capabilities available within the Division and elsewhere in the Center.

The research reported in previous years on the negative ion chemical ionization (NICI) of polynuclear aromatic hydrocarbons provided a useful analytical capability. Continuation of this work is being undertaken by Dorothy Falcone, a graduate student at The American University, who has joined the group as a Guest Scientist.

Investigation of the laser induced photodissociation of ions as a technique for the determination of the structure of large molecules has been terminated. The project succeeded in producing the first observations of the photodissociation of ions generated by field ionization, field desorption, and fast atom (cesium ion in our case) bombardment. The limits of our present instrumentation and straightforward approach had been reached. Alternate approaches including chemical derivatization to increase absorptivity and the construction of a high intensity resonant cavity would require currently unavailable personnel and equipment. Other laboratories now have pursued photodissociation as a technique for structure determination. One particular variation of this technique has practical applications.

In the year ahead we plan to continue work on many of the projects with which the group is presently involved. Specific efforts will include: completion of the work required for the reissue of SRM 916, Bilirubin; completion of the drugs of abuse SRM for cocaine; the issue of SRM 1952, Cholesterol in Freeze Dried Human Serum;

measurements required on a material to replace SRM 909, Human Serum; the assignment of values on CAP survey materials; the set up of a reference method for protein for the CAP; refinement of the analytical method, developed a year ago, for measuring the dose of radiation to which meats have been exposed; and, application of collision induced dissociation and thermospray on the triple quadrupole mass spectrometer for high accuracy quantitation. Longer range plans include: the development of a definitive method for triglycerides in serum; the quantitative determination of DNA adducts; and the adaptation of photodissociation experiments to instrumentation other than the high resolution double focusing magnetic instrument presently used.

The instrumentation available to the group improved near the end of last year with the installation of a completely equipped triple quadrupole mass spectrometer and we have now learned to use the LC/MS (thermospray ionization) and collision induced dissociation techniques not previously available to us. The group presently has five mass spectrometers: the triple quadrupole instrument; a "mass selective detector," a GC/MS with electron impact capability only; another quadrupole GC/MS instrument, a magnetic sector GC/MS instrument, and a high resolution double focusing instrument. These presently provide us with all of the capabilities we need, with the exception of full scanning at high resolution. The oldest instrument, at 14 years, is the magnetic GC/MS on which the definitive methods are dependent. However, provision has been made, in the agreement with the CAP, for funding to assist with replacing this instrument in a few years.

The personnel in the group has changed considerably over the last year. We are seeking one new mass spectrometrist for the group and also postdoctoral candidates whose interests are compatible with our interests and programs.

Edward White V, Group Leader; Alex Cohen, Polly Ellerbe, Stanley Meiselman, Lorna T. Sniegoski, Susan Tai, and Michael J. Welch.

B. Selected Technical Reports
(Organic Analytical Research Division)

1. Investigation of the Relationship between Stationary Phase Thickness and Selectivity for Isomeric Compounds in Reversed-Phase Liquid Chromatography

L.C. Sander and S.A. Wise

Differences in retention behavior of supposedly similar or identical stationary phases have prompted investigations concerning the influence of bonded phase parameters on retention. Solute retention in reversed-phase liquid chromatography is often described in terms of solvophobic interactions between the solute, the mobile phase, and the stationary phase. Unfortunately, this model does not adequately explain stationary phase contributions to selectivity. In previous work we have demonstrated that differences exist in selectivity for the separation of polycyclic aromatic hydrocarbons (PAH) on monomeric and polymeric C_{18} stationary phases. In our present investigation, we studied the effect of alkyl phase length on selectivity for phases prepared using both monomeric and polymeric modification chemistries. This work has added to our understanding of retention mechanisms for PAH and has implications that may help to improve separations of other classes of compounds.

Monomeric and polymeric phases were prepared with chain lengths ranging from C_8 to C_{30}. Chromatographic properties of each column were assessed with PAH probe solutes. A mixture of three PAH (benzo[a]pyrene, BaP; phenanthrophenanthrene, PhPh; and tetrabenzonaphthalene, TBN) has been found to be particularly useful in classifying phase selectivity. This mixture has been used in past work to distinguish monomeric- and polymeric-like selectivity in over 25 commercial C_{18} columns. Recently, we proposed the use of this mixture as a column evaluation mixture to determine the selectivity of C_{18} phases. For the alkyl phases of different chain lengths, overall selectivity toward PAH increased with increasing chain length (phase thickness). For both monomeric and polymeric synthetic routes, short chain length phases exhibited monomeric-like selectivity, whereas polymeric-like selectivity was exhibited for long chain length phases. The biggest difference in retention behavior for the two phase types was observed for phases of intermediate length, i.e., C_{18} phases. Small angle neutron scattering (SANS) was used to directly measure differences in phase thickness using a technique known as contrast variation. The bonded phase materials were placed in solvents containing known hydrogen/deuterium ratios (methanol/methanol-d_3). By matching the scattering length density of the silica, scattering from the pore structure was eliminated and information about the bonded phase thickness was obtained. Polymerically bonded C_{18} phases were found to be about 50% thicker than monomerically bonded C_{18} phases.

The ability of a particular column to discriminate between PAH isomers (shape selectivity) has been described by a schematic representation of the bonded phase referred to as the "slot model". The retention of narrow planar PAH in preference to square, nonplanar PAH can be visualized in terms of penetration of the molecules into imaginary slots in the bonded phase. Because narrow molecules will fit into these slots more completely than bulky molecules, solute-bonded phase interactions are stronger and retention is greater. Phase thickness adds a third dimension to the picture. Extending this model, phases with deep slots (thick phases) will exhibit more shape selectivity than phases with shallow slots (thin phases).

This study has demonstrated that phase selectivity toward PAH can be controlled by altering phase thickness as well as phase type. Separations carried out on other classes of solutes (e.g., carotenoid compounds) have suggested that "thick phases" may, in general, have potential for enhanced resolution of structural isomers. Our studies of stationary phase characteristics that affect selectivity in reversed-phase liquid chromatography are continuing.

2. Evaluation of the Quantitative Capabilities of Thermospray LC/MS

R.G. Christensen, P.M. Ellerbe, and M.J. Welch

The combination of liquid chromatography with mass spectrometry (LC/MS) is a powerful new tool for the analysis of organic compounds. This technique has been used widely to identify and characterize substances which are difficult or impossible to analyze by gas chromatography. The application of LC/MS to quantitation has been much more limited, in part because of large imprecision caused by fluctuations in the signal level that are generally observed. One promising approach to precise quantitation by LC/MS involves the use of stable isotope labeled internal standards. These compounds would co-elute with the analyte and thereby allow the affect of source pressure fluctuations to be minimized. We have been investigating this approach to determine if LC/MS can be used to accurately and precisely quantify analytes which are difficult to measure by other techniques.

The determination of uric acid in serum by LC/MS was chosen for investigation. Reconstituted serum (SRM 909) was spiked with a known amount of uric acid-$^{15}N_2$ and treated with trichloroacetic acid to precipitate protein. Fifty microliters of the supernate were then injected directly onto a C-18 LC column which was interfaced to a triple quadrupole mass spectrometer via a thermospray device. The best results were obtained when the thermospray ion source was tuned for best signal stability rather than for maximum sensitivity. The eluting solvent was an aqueous solution of 0.075 M ammonium acetate and 0.003 M tetrabutylammonium hydroxide adjusted to pH 5.2. The (M-H)- ions for the unlabeled and labeled forms of uric acid were measured and their ratio calculated. To determine the quantity of uric acid in the serum, such ratios were compared with ratios from uric acid standard solutions spiked with a concentration of labeled uric acid similar to that in the samples. The results for the three serum samples tested were within about 1% of the certified value (81 ppm) determined by the isotope dilution/gas chromatography/mass spectrometry definitive method. The LC/MS method is less precise (coefficients of variation about 1%) than the definitive method, (c.v. ~0.3%) but requires far less sample pretreatment.

The evaluation was carried one step further as a test for specificity. The triple quadrupole mass spectrometer is designed to allow collision-induced dissociation (CID) of ions. Therefore, we selected the (M-H)- ions from LC/MS, performed CID on them, and measured the intensity of specific fragment ions. This process (LC/MS/MS) eliminates most likely interferences, thereby minimizing the probability of bias. The LC/MS/MS results agreed well with the LC/MS and GC/MS results.

These evaluations demonstrate that the combination of isotope dilution with thermospray liquid chromatography/mass spectrometry can provide accurate and precise results and should provide both another tool for use in the certification of SRMs and a means for the determination of many substances that are not readily determined by GC/MS.

3. Thymine-Tyrosine Crosslinks: The Identification of a New Group of Radiation-Induced Compounds of Potential Biochemical Importance

S.A. Margolis, B. Coxon, E. Gajewski*, and M. Dizdaroglu*

DNA-protein crosslinks have been induced in both procaryotic and eucaryotic cells by UV, X-, and gamma radiation. The frequency and repair of such crosslinks is directly proportional to the dose of radiation and the survival of irradiated cells. The methods for quantifying the formation of crosslinks is complex, lengthy

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*Center for Chemical Physics.

and prone to error. The identification of the chemical nature of the crosslinks and the development of chemical methods of analysis provide a solid basis for the development of a biochemical method for radiation dosimetry and the measurement of DNA repair.

In a model system composed of an irradiated mixture of tyrosine and thymine we have isolated thymine-tyrosine crosslinks using liquid chromatography. The mass spectrum of the crosslinked product revealed a fragmentation pattern characteristic of such a dimer, and the proton and carbon NMR spectra proved that the dimer consisted of equal amounts of tyrosine and thymine with a carbon-carbon bond between the methyl group of thymine and the 3-carbon of the phenolic ring of tyrosine. By high resolution mass spectrometry, the molecular weight of the dimer ion was within 5 milli-mass units of that expected. These results have been accepted for publication in **Biochemistry.** We have subsequently demonstrated that the identical compound is formed upon the irradiation of calf thymus nucleohistone and that the formation of this dimer is proportional to the dose of gamma radiation between 14 and 300 Gy. This would suggest that it is possible to detect these crosslinks in animal tissues exposed to 1×10^2 to 1×10^5 Gy and to use this method as a radiation dosimeter. In addition, Gajewski, et al. [(1988), have identified by gas chromatography-mass spectrometry, the occurrence in irradiated nucleohistone of the crosslinks of thymine and the amino acids glycine, alanine, valine, leucine, isoleucine, and threonine. These show a similar dose-concentration response and may also serve as alternative or secondary dosimeters. However, the advantage of the tyrosine-thymine crosslink and other crosslinks over monomer products, such as ortho-tyrosine, is their high molecular weight, thus reducing the possible interference from low molecular weight compounds when single-ion monitoring gas chromatography-mass spectrometry techniques are used for identification and quantitation.

The preliminary results from their investigation provide a chemical basis for the measurement of the effect of radiation on cellular nuclear material, particularly nucleohistone, and thus open up several new avenues for research which are:

(1) The in-vitro formation, isolation and characterization of other amino acid nucleic acid dimers (some of which have been detected in gamma irradiated calf thymus nucleoprotein) by use of the methods described for the thymine-tyrosine dimer;

(2) The demonstration of the occurrence of these dimers in gamma radiated viruses, cells and tissues;

(3) The development of a method of biochemical dosimetry for irradiation exposure of animal and plant cells and tissues.

4. Liposome-Enhanced Flow Injection Immunoanalysis

A.L. Plant, L. Locascio-Brown, M.V. Brizgys, and R.A. Durst

Immunoglobulin (antibody) proteins are potentially powerful analytical reagents because of several important characteristics. They typically bind their ligands with very large affinity constants, in the range of 10^{-5} M^{-1} to 10^{-10} M^{-1}, and in addition can exhibit a high degree of specificity in molecular recognition of their ligands. Antibodies can be prepared, for example, which can distinguish between optical or positional isomers of otherwise identical molecules. As a result, they are extremely effective agents for isolating and identifying analytes of interest which are present in complex mixtures. Antibodies can be produced against almost any molecule, and cells producing monoclonal antibodies can be stored for long periods of time to ensure a constant supply of antibody reagent with discrete affinity and specificity characteristics.

The interaction between antigens and antibodies is the basis of sensitive diagnostic techniques such as radioimmunoassay (RIA) and enzyme-linked immunosorbant assay (ELISA). Although these techniques are very sensitive and widely used, they can be time-consuming and technically cumbersome, and are only semi-quantitative. The optimal immuno-based assay should be fast, quantitative, and able to be calibrated and automated.

Our current approach to the development of such an analytical system is a combination of the technique of flow injection analysis (FIA) with immunochemistry, which we call flow injection immunoanalysis (FIIA). FIA is a continuous-flow method based on the introduction of a sample aliquot into a moving nonsegmented carrier stream. All introductions and directions of flow are determined by a series of microprocessor-controlled solenoid valves.

Immobilization of antibodies which bind an analyte of interest in an FIIA reactor is the first step in developing a reusable, automated immunoanalyzer. The basis of our immunoreactor is a small column of solid glass beads which have been prepared by derivatizing with monofunctional aminopropylsilane. We have characterized the stability of this silane coverage under flowing conditions and found that less than 1% of the silane is lost during 24 h of continuous flow in pH 7 aqueous buffer. The amino group of silane is then derivatized with a bifunctional reagent, to which an antibody F(ab)′ fragment is then attached. We are currently testing some novel chemistry which will provide stable, oriented, and active immobilized antibody protein. We are using fluorescence techniques as well as radiolabel approaches to characterize antigen binding activity of antibody in solution, for the purpose of quantifying the effect of immobilization.

Detection and quantitation of the interaction between analyte in a sample and the immobilized antibodies on the immunoreactor column are mediated through the use of lipid vesicles (liposomes). Liposomes are prepared with approximately 10^5 fluorescent molecules contained within each. When liposomes which are appropriately derivatized, compete with analyte molecules in a sample for binding to immobilized antibodies, every liposome which does not bind, due to the presence of a bound analyte molecule, flows downstream into a fluorescence detector. We have developed a generic method of derivatizing liposomes so that it is relatively easy to prepare reagent liposomes for different analytes. A small molecule, biotin, is attached to the polar headgroup of some of the phospholipid molecules comprising the liposome membrane. These biotinylated liposomes are then attached to biotinylated analyte-analogue molecules through the protein, avidin, which has multiple binding sites for biotin.

The practical application of an automated, reusable, and quantitative analytical system of such sensitivity and specificity should have enormous impact in the areas of clinical, environmental, and industrial measurements. In addition, this approach poses serious challenges in the area of antibody protein chemistry, and the results of this work is of direct importance to all immobilized antibody applications, including affinity chromatography and extracorporeal detoxification. In the area of FIA, the study of liposomes as model systems for macromolecules and microorganisms in flowing systems has already received attention. Work on derivatization of liposomes is also applicable to other forms of immunoassay as well as to the area of drug delivery.

5. Laser-Induced Modification of Electrode Surfaces

W.A. MacCrehan

The electrochemical current response at a solid-surface electrode is highly dependent on the condition and history of the surface. Many procedures have been developed to provide a clean, reproducible surface at glassy carbon electrodes. However, in many systems the current resulting from changing the applied voltage still shows a kinetically sluggish response. A new approach to cleaning and activating carbon electrodes has been demonstrated recently by Prof. Richard McCreery of Ohio State University, who applied a single, high-power laser pulse to the surface of the electrodes. The pulse energy is sufficient to desorb all impurities and to generate a short-lived plasma at the surface. Not only is the electrode made atomically clean by removing impurities and surface oxides, but some restructuring of the graphitic crystal structure may occur. The transfer of electrons to organic molecules in solution is often substantially enhanced at the activated surface, as evidenced by a lower over-potential required to cause the electrochemical reaction to occur, and by enhanced current signals. For example, the oxidation of ascorbic acid (vitamin C) occurs at a potential of +700 mV at a conventionally polished carbon electrode, but at the laser-activated surface the electrochemical process occurs at a potential of +350 mV with improved current response. This allows detection of ascorbic acid with improved selectivity and sensitivity.

Until now, the reproducibility of the activation process using a single neodymium:YAG laser pulse has been relatively poor, caused by pulse-to-pulse variations and spatial inhomogeneity of the laser beam intensity. We are investigating ways to improve the activation process. Another difficulty has been the limited lifetime of the activation, which lasts for only a few minutes. Chemical reactions that deactivate the surface are currently under investigation so that this process might become better understood. In particular, the formation of thin polymeric films to cover the electrode with an inert layer is under study. Following this treatment, high-intensity micron-sized laser pulses could be rastered over the surface creating activated "microelectrodes arrays" on the surface of the larger, easily manipulated electrode. Microelectrodes have significantly enhanced the ratio of the desired analytical signal to background noise, which makes it possible to detect smaller quantities of material.

Additionally, since only a very few organic analytes have been tested, we are investigating the application of activated electrodes to the detection of a diversity of organic compounds. A particularly attractive approach will be to use the laser-activated electrodes in flowing streams such as those coming from a liquid chromatograph. Periodic laser activation could enhance the sensitivity and selectivity of the detector.

6. Synthesis and Characterization of a Novel "Capped" Cobalt(II) Metalloporphyrin: Electrochemical Evidence for a Mixed Coordination Sphere about the Central Metal Ion

E.A. Blubaugh and R.A. Durst

The chemical modification of electrodes imparts specific and predictable properties to the surface of these electrodes. One avenue of research involves the utilization of these modified electrodes as electrochemical detectors in combination with liquid chromatography. Parameters such as film stability and fast-ion/electron transport through the film are important, but the chemical nature and stability of the incorporated electrocatalysts are just as important. Porphyrins are an obvious choice for immobilized electrocatalysts because of their robust chemical nature, excellent catalytic behavior and variability in their redox potentials as a function of ligand substituents.

Recent work in the area of porphyrin synthesis has resulted in the discovery of a type of porphyrin, where, by synthetic design, one of the two axial sites is encumbered. These porphyrins provide a binding site which is analogous to the binding site for oxygen in hemoprotein biomolecules. Our contribution to this family of "capped" porphyrins is the synthesis of a new member, which differs from the previous members by changing the capping portion from benzene to pyrazine. The pyrazine moiety should change the chemical nature of the binding pocket and will allow fundamental studies on the chemical influence that the pocket has on metal-centered chemical reactions for these porphyrins. In addition, these "capped" porphyrins have a built-in size exclusion due to the capping moiety, which will also be beneficial to their use a catalysts.

The metalloporphyrin of interest is the cobalt(II) derivative of these "capped" porphyrins. The cobalt(II) derivatives display a reversible and stable redox chemistry associated with the cobalt(II)/cobalt(I) couple. However, under appropriate conditions, such as in the presence of organohalides, the Co(II)/Co(I) couple becomes irreversible due to the reaction of the nucleophilic Co(I) species with the carbon-halide bond. Our capped cobalt metalloporphyrins (both benzene and pyrazine derivatives) display reversible redox behavior for the Co(II)/Co(I) couple with a formal potential of -0.930 volts vs. SSCE. The pyrazine capped porphyrin shows an additional wave at -1.035 volts vs. SSCE. This second redox couple is the reduction of a cobalt(II) center, which has been stabilized by coordination of the pyrazine cap in either a side-on or end-on orientation. The particular condition of axial binding for pyrazine will require additional spectroscopic work.

For both cobalt metalloporphyrins, the Co(I) species shows a marked sensitivity to the presence of an organohalide (i.e., ethylene dibromide, EDB). The redox couple becomes totally irreversible with a plateau for the electrolysis current in the potential range of -1.1 to -1.3 volts vs. SSCE. These results indicate that the cobalt(I) does indeed reduce the organohalide, and does so in a catalytic manner, since the direct reduction of EDB occurs at -1.750 volts vs. SSCE.

Future work will include the characterization of these novel metalloporphyrins incorporated in polymer films and their evaluation as electrocatalysts for the reduction of organohalides.

7. Adaptation of Definitive Method Technology for the Certification of Food-Related Reference Materials

P.M. Ellerbe, L.T. Sniegoski, M.J. Welch, and E. White V

For over a decade, NIST has been involved in the development of definitive methods for serum constituents. These methods are highly accurate and precise, and are used to certify analyte concentrations in reference serum pools. The technique on which the methods are based is isotope dilution/gas chromatography/mass spectrometry. Samples are spiked with a stable isotope labeled form of the analyte of interest. After an equilibration period, the samples are processed to isolate the analyte and internal standard from the matrix. The analyte is derivatized and injected into a gas chromatograph/mass spectrometer system. The ratio of unlabeled to labeled analyte is determined by comparing of ion abundance ratios for each sample with those of standard mixtures. Great care is exercised in the sample preparation and measurement steps, resulting in data with small imprecisions and no evidence for systematic bias. These methods, which have been thoroughly tested on serum samples, are now being adapted for determining analytes in other matrices.

Research into the relationship of dietary intake and health status has generated great interest in both the scientific community and the general population. Cholesterol, which has been linked to risk of coronary heart disease, is a food component of major concern. We have adapted our definitive method for serum cholesterol to the certification of cholesterol in three food-related matrices. Such materials can then serve as a means for evaluating the accuracy of methods used for determining the composition of foods.

The first food-related material in which cholesterol was determined was SRM 1563, cholesterol and fat-soluble vitamins in coconut oil. This SRM consists of a two materials, one natural oil and one fortified with a known amount of cholesterol. The certification of the fortified oil was straightforward with good precision, and confirmatory measurements provided evidence for the absence of bias in the measurement process. A combination of the GC/MS data and gravimetry yielded a certified value of 64.2 ± 0.6 mg/100 g oil. Because the level in the natural oil was very low, we were not able to do confirmatory measurements and the precision was not as good as we normally observe. The certified concentration for this material is 0.344 ± 0.014 mg/100 g oil. Nevertheless, the precision for both materials exceeded the recommended guidelines for such a material.

The second material is a freeze-dried composite food, representative of a typical American diet. This material was prepared by the U.S. Dept. of Agriculture and will have certified values for a variety of organic and inorganic constituents. Certification of the cholesterol content is in progress. In addition, we will investigate the modification of our definitive method for serum glucose to determine glucose, fructose, and possibly other sugars in this material.

The third material is a composite freeze-dried whole egg material. For other matrices we have used a standard alkaline hydrolysis to free cholesterol from its esters. The AOAC method for cholesterol in eggs calls for an acid hydrolysis. We studied both approaches and found evidence that cholesterol is partially destroyed by the acid hydrolysis. The alkaline hydrolysis was found to be complete, and thus, will be used for the certification measurements.

The extension of definitive method technology to food matrices provides a means of accurately and precisely certifying important analytes in materials that can then be used to evaluate the performance of more routine methods used for making health and nutritional decisions.

8. Determination of PCB Congeners in Complex Matrices Using Two-Dimensional Gas Chromatography

F.R. Guenther and S.N. Chesler

A multidimensional gas chromatographic technique has been developed to quantitatively determine individual PCB congeners. This method utilizes a high resolution capillary precolumn to separate the PCB congeners according to volatility. Pure PCB congeners are chromatographed to verify elution time, and published Retention Indices alert us to possible coeluters. The specific congener and co- or closely eluting compounds are then cut from the effluent of this column, using a differential pressure switch, and transferred to the head of the second column, which does the final separation of the closely eluting congener pairs. The second column is a high resolution capillary column coated with an immobilized liquid crystal phase. The separation on this column is based on molecular shape and, to a lesser extent, polarity. The effluent from the second column flows into a Hall Electrolytic Conductivity detector which is sensitive to, and selective for, chlorinated compounds.

It has been demonstrated that this two-dimensional method provides the capability for identifying (based on retention) and quantifying important PCB congeners, that are known to coelute with other congeners in every other known chromatographic system. It is hoped that this system will provide the primary means for certifying selected PCB congeners in two sediment-based SRMs during the coming year.

Several improvements to this method are contemplated for the near future. This includes the substitution of ECD detectors for the present detectors to improve the detection limits of the system, and the possible use of the mass selective detector to improve the specificity of the method. Also possible is the use of a 60 m precolumn that will enable much higher accuracy in the timing of the heartcut. In the coming year this approach will be applied to other analyte groups where close elution of isomer pairs make quantitative analysis difficult, if not impossible.

9. Organic Chemical Markers for the Identification of Residential Wood and Mobile Source Combustion

B.A. Benner, Jr., S.A. Wise, and A. Sheffield

In an effort to better delineate source contributions to atmospheric particulate matter at an urban site, a project was undertaken to determine if there were any differences in the relative concentrations of polycyclic aromatic hydrocarbons (PAH) in atmospheric particulate matter from different combustion sources. The dichloromethane extracts of three ambient air particulate matter samples from the Integrated Air Cancer Project (IACP), sponsored by the Environmental Protection Agency, were characterized for their PAH content by combined liquid and gas chromatographic techniques, including gas chromatography with mass spectrometric detection (GC-MS). These three samples were selected to be representative of samples influenced by (1) high residential wood combustion (RWC), (2) mixed RWC and mobile source combustion, and (3) high mobile source combustion. Concentrations of 23 analytes were determined in the PAH fractions of the three IACP extracts. When compared on a µg/mg residue basis, the concentrations of most of the PAH in these three samples were of a similar magnitude, particularly the PAH with molecular weights greater than 226 amu. The four most abundant species in the PAH fraction of the RWC sample were tentatively identified as the methyl ester of dehydroabietic acid, 1-methyl-7-isopropylphenanthrene (retene), the co-elution of the methyl ester of abietic acid (tentative) and a methylfluoranthene or methylpyrene isomer, and 1,7-dimethylphenanthrene (pimanthrene). The four most concentrated species in the PAH fractions of the mixed source sample and the mobile source sample were the methyl ester of dehydroabietic acid, the co-elution of benzo[b, j and k]fluoranthenes, benzo[ghi]perylene and retene. Derivatives of abietic acid in wood combustion extracts have been reported previously. The presence of retene (1-methyl-7-isopropylphenanthrene) in wood smoke has also been reported and it has been suggested that it could serve as a residential wood combustion marker for resinous woods (conifers). Single-ion chromatograms of m/z 192 (dimethyl- and ethylphenanthrenes) for the RWC sample and samples collected in a highway tunnel display similar relative levels of dimethylphenanthrene isomers except that the relative concentration of 1,7-dimethylphenanthrene is much higher (a factor of 10) in the RWC compared with the tunnel samples. The predominance of 1,7-dimethylphenanthrene in the RWC sample suggests that this alkylated phenanthrene may also serve as a marker for residential wood combustion. The identification of chemical markers indicative of the influence of residential wood combustion and mobile source emissions for these samples as determined by GC-MS analysis of the PAH fraction was consistent with the ^{14}C source apportionment analyses performed on these same samples. The use of these chemical markers to distinguish source contributions to ambient particulate matter will be investigated further with additional comparisons of ^{14}C and GC-MS analyses of ambient particulate matter extracts.

10. Proteins of Human Liver: Two-Dimensional Gel Electrophoretic Mapping of Human Liver Tissue

J.J. Edwards and D.J. Reeder

The assessment of liver function is of crucial importance in clinical chemistry. Evaluation of normal liver function or the detection of malfunctioning processes has required the development of numerous assays which indirectly monitor function by measuring the activities of selected enzymes or by detecting components released from damaged cells. These assays, however, offer little in the way of describing the complex nature of a human tissue or the processes occurring within that tissue that are either the cause or result of abnormal function. A better understanding of tissue function requires that the complex relationship between individual cellular components be defined from a molecular viewpoint.

Analysis of human liver tissue at the molecular level requires the use of reproducible high-resolution separation techniques, sensitive detection methods, and accurate recording and data handling capabilities.

These requirements are best met by two-dimensional gel electrophoresis, silver staining, and computerized image analysis. Also required for this type of study is the availability of a large sampling pool of tissue that has been obtained and processed in a rigidly prescribed manner. This requirement was met through the use of human liver tissues from the NIST/EPA National Biomonitoring Specimen Bank, which currently has an inventory of over 500 samples. Tissue stored in the Specimen Bank are samples taken at the autopsy of accident victims. Samples were taken under conditions which were specifically designed to prevent contamination and degradation. Samples used in this study were, upon collection, frozen in liquid nitrogen, homogenized, and stored in Teflon containers at liquid nitrogen temperatures. Prior to being added to the Specimen Bank inventory, all samples underwent routine pathological examination. Only samples found to be free of recognizable diseases including hepatitis, were selected for storage. Selected samples were removed from liquid nitrogen storage and maintained at -80 °C until analyzed. Patient history, including documented cause of death, was available for all samples analyzed.

We have analyzed, by two-dimensional electrophoresis protein mapping, a limited number of samples of presumably normal human liver tissue. Unlike easily obtained samples of human origin such as blood components and other body fluids, the direct analysis of organ tissue has been limited by the unavailability of normal tissue samples, with the exception of skeletal muscle and brain. This study on human liver tissue was prompted by the large number of samples made available by the Specimen Bank. Some of the questions asked during the course of this study were: (1) Can samples taken at autopsy be used to construct reliable high-resolution protein maps?; (2) Can procedures designed for the analysis of other tissues be modified to yield reproducible solubilization and separation of protein components?; (3) How many proteins or protein subunits can be reproducibly resolved and visualized using two-dimensional electrophoresis and silver staining?; (4) Can any known cellular proteins be identified?; and (5) Are contaminating proteins present and do they interfere with the analysis of cellular components?

Homogenized frozen tissue was solubilized, mixed, and centrifuged to prepare a known concentration of sample. First dimension isoelectric focusing was performed on ten samples in duplicate using the ISO apparatus before they were electrophoresed at 600V for a total of 10,000 volt-hours. Electrophoresis on slab gels (second dimension) in the presence of sodium dodecyl sulfate (SDS) was performed with the DALT apparatus. Proteins were fixed, stained and developed using a modified silver staining procedure.

We have scanned the two-dimensional gels by use of a high-resolution imaging system and have identified a number of comparison proteins for further analysis. Correlation of protein spot similarities and differences are being pursued as a database system is being established.

Characterization of the protein composition of normal liver tissue should assist future research efforts in resolving issues relating to such topics as; (1) the identification of protein gene products common to a distinct tissue type; (2) the identification of major normal human variants; (3) normal variability of protein species found in the population; and (4) differential gene expression resulting from disease, disease treatment, toxicity, and aging.

11. Results of an Interlaboratory Study to Assess Reproducibility of Rehydratable Isoelectric Focusing Gels

K.L. Richie and D.J. Reeder

During the past year, we conducted an interlaboratory collaborative study to test the effectiveness of rehydratable gels in obtaining consistent patterns with standard protein preparations. Rehydratable gels, which represent a relatively new type of support medium for isoelectric focusing, were developed in part to meet the demand for convenience, flexibility and reproducibility in a gel support system. Rehydratable gels, unlike in-house prepared gels, can be prepared under well-standardized conditions, thus minimizing a number of undesirable or unknown characteristics; the end result being a more defined gel that requires no prefocusing because of the extensive washing to remove any by-products of polymerization. A major advantage of using these rehydratable gels is the low initial current obtained, thereby allowing the application of higher voltages which result in increased resolution. These gels are easily rehydrated in an ampholyte-glycerol mixture and can be ready for focusing in as little as thirty minutes. Furthermore, the dried gels may be stored for over a year at room temperature without any loss in resolving capabilities.

In this two-part study, each of the participating laboratories was provided with a package containing a standard protein sample, rehydration media with instructions, rehydratable gels and a protocol. In the first phase of the study, laboratories were allowed to run gels by their existing methods or by whatever method they felt would give the best results. In comparing these laboratory results, we noted large variations in the protein band patterns for the same protein. These differences were caused mostly by the wide variety of operating procedures that were employed. In the second phase of the study, participants were provided with a commercially available set of pI charge markers to ensure sample uniformity and were asked to closely follow a set of specified running conditions. Overall, the results from the second study were more uniform than those in the first study, thus indicating the importance of standardizing as many of the running conditions as possible. Differences could be attributed to: (1) voltage gradient applied, (2) temperature during the run, (3) electrode separation distance, (4) relative humidity at the time of the run and (5) type of apparatus used. Currently, these gels are being scanned by densitometry from as many different types of scanners as possible. Results will be statistically compared and reported.

12. Two-Dimensional POMMIE Carbon-Proton Chemical Shift Correlation ^{13}C NMR Spectrum Editing

B. Coxon

In an extension of previous work on two-dimensional (2D) POMMIE J(CH)-resolved ^{13}C NMR spectrum editing [B. Coxon, Magn. Reson. Chem. 26 (1988), in press; POMMIE = phase oscillations to maximize editing], we have investigated the feasibility and limitations of 2D POMMIE pulse sequences for the separation of carbon-proton chemical shift correlation ^{13}C NMR spectra into CH, CH_2, and CH_3 subspectra (2D spectrum editing). The purpose of these experiments is to simplify the 2D NMR spectra of complex molecules, thus facilitating spectral interpretation, assignment, and the separation of overlapped peaks.

Our initial studies have focused on unique pulse sequences to optimize signal acquisition. Selected carbohydrate, macrolide antibiotic, and tri- and tetra-peptide derivatives have been used as model compounds in these studies. Initially, the raw data for shift correlation editing were acquired as three 2D data matrices, using the phase angle set ϕ = 30°/90°/150°, as we have used previously for 2D DEPT and 2D POMMIE J(CH)-resolved ^{13}C NMR spectrum editing. This allowed the shift correlated CH, CH_2, and CH_3 subspectra to be computed as 1:1 linear combinations of the three 2D data matrices.

By this means, very good 2D carbon-proton chemical shift correlated CH and CH_3 subspectra could be obtained, but, for typical carbohydrate and peptide derivatives, the generation of good CH_2 subspectra was found to be more difficult. The residual CH and CH_3 signals in the CH_2 subspectra were often unexpectedly large. This effect appears to be due partly to the fact that the methylene protons in these derivatives are commonly non-equivalent, due to the presence of asymmetry in the molecules. The combined effect of chemical non-equivalence and mutual spin coupling of the geminal methylene protons reduces the intensities (peak heights) of the cross peaks in the CH_2 correlation subspectra by a factor of ≈ 4, so that the intensities of the CH and CH_3 residues appear to be more prominent by a factor of ≈ 4. These limitations also apply to 2D DEPT shift correlation editing. For 2D POMMIE, it was also observed that use of the value $\phi = 90°$ did not yield the best CH subspectrum. The use of these methods has generally yielded 2D POMMIE subspectra of better quality, for both J(CH)-resolved and carbon-proton shift correlations.

We have also studied a pulse sequence for 2D POMMIE chemical shift correlation editing which incorporates a BIRD (bilinear rotation decoupling) sequence for ^1H-^1H decoupling in the F_1 dimension and a composite ^{13}C 180° pulse for improvement of sample excitation, and where the symbols have the same meaning as before. This sequence has been tested on oleandomycin, which has yielded CH_2 subspectra in which several of the methylene correlation crosspeaks are sharper due to removal of vicinal ^1H-^1H spin couplings in the F_1 dimension.

In summary, although the 2D POMMIE method has several advantages, one particular disadvantage is that the theoretical dependence of ^{13}C intensities on the phase shift ϕ is not followed, with the result that adjustment of one or more values in the phase angle set is required. It appears, however, that the generation of good CH_2 chemical shift correlation subspectra by either the 2D DEPT or 2D POMMIE methods requires use of more time-consuming Pascal computations in the floating-point mode.

13. QA Activities for the National Cancer Institute: Establishment of an Accuracy Base for Measurements of Micronutrients in Serum

J. Brown-Thomas, R.G. Christensen, N.E. Craft, M.C. Kline, W.E. May, W.A. MacCrehan, R. Paule, and R. Schaffer

For the past four years, the Center for Analytical Chemistry has operated a multi-component quality assurance program for laboratories that measure serum and plasma levels of selected fat- and water- soluble vitamins, zinc and selenium as part of investigations supported by the National Cancer Institute, Division of Cancer Prevention and Control, to study the possible cancer-prevention benefits of these micronutrients in populations of humans at high risk of contracting certain forms of cancer.

Two of the main components of the program have been (1) interlaboratory proficiency testing, and (2) reference materials development. Serum-based samples with assigned values for the target analytes are distributed to participating laboratories (10-35 depending on the analyte) three times during the course of the year. The labs receive feedback concerning their performance and suggestions for improving their measurement capabilities on an as needed basis. The results from the proficiency testing exercises (round robins) are used to establish a laboratory performance database for use by NCI to evaluate the quality of the analytical data from which clinical conclusions are to be drawn. In addition to assessing lab performance, the program is designed to provide a framework for assisting laboratories in improving their measurement capabilities. During the past year, serum-based reference materials with assigned values for retinol, alpha-tocopherol and beta-carotene were developed and distributed, along with instructions for their use, to the labs for use as controls. The assigned values were based on the mean from the interlaboratory grand average and two independent NIST measurement procedures. The uncertainty associated with the assigned value derived from this process was in the 4-6% range.

Use of the value-assigned reference materials provided to the labs had a significant impact on the quality of the data obtained from the round-robin exercise conducted several months after their distribution. For retinol measurements, the relative standard deviation of the interlaboratory measurement had been 12-15% for the past two years. The relative standard deviation of results from the most recent round robin dropped to 8-9%. Approximately 67% of the participating labs reported results that were to be acceptable (i.e., results on all five sera provided were biased by <15%). In the previous round robin, results from five laboratories were unacceptable (data biased by >30%). In the most recent exercise, three of these five laboratories reported results with biases of 10%; one laboratory dropped out of the program; one laboratory again reported unacceptable results. The one laboratory that again reported unacceptable results <u>did not</u> run the control materials.

For alpha-tocopherol measurements, the relative standard deviation for the interlaboratory measurements was 12-15% for the past year. The relative standard deviation of results for the most recent round robin dropped to 8-10%. Approximately 60% of the participating laboratories reported results that were acceptable. None of the laboratories reported results that were unacceptable.

For beta-carotene, interlaboratory precision improved from 20% to 15% in the most recent round robin. In the most recent round robin, the four labs that reported unacceptable data <u>did not</u> run the control materials provided to them.

The data from the most recent fat-soluble vitamins round robin exercise clearly demonstrate the benefit of value-assigned reference materials in improving interlaboratory measurement quality.

14. <u>Preliminary Investigations Directed Toward the Development of Reference Materials for DNA Adducts in Body Fluids</u>

D.J. Reeder and M.C. Kline

As part of the Department of Energy's interest in adverse effects of environmental pollutants from fossil energy sources, we have started a project to develop reference materials for DNA adducts. Preliminary studies included literature searches and a visit to several national laboratories to assess the analytical methods being developed for sensitive detection of DNA adducts. We have also established methods for separating DNA by HPLC and have qualified a system for DNA characterization by electrophoresis.

For highly sensitive measurements of PAH-DNA adducts, fluorescent line narrowing is performed with a high-powered pulsed dye laser with the sample cooled to 4 K with liquid helium at Ames Labs. At Battelle, researchers are performing separations by reversed phase LC with adduct detection by on-line fluorescence measurements. Measurements are also made by gas chromatography on derivatized adduct materials (measuring tetrols), with detection by a mass-selective detector. At Argonne Labs, the techniques more frequently involve in hemoglobin. They use the diol-epoxide of benzo[a]pyrene (BAP) to modify the beta-chain of hemoglobin. Shifts in retention time are observed by HPLC with fluorescence detection.

As a starting point for providing materials to other laboratories, we plan to provide authentic DNA with varying amounts of adducts starting with BAP, followed by chrysene and 5-methyl chrysene. In addition, we plan to provide different sizes of DNA, and DNA adducts, given our present capabilities of separating DNA by HPLC and characterizing electrophoretically (by size) yeast chromosomal pieces of DNA.

We also may consider making DNA adducts by a method employing rat liver homogenates. Rat liver is made into a homogeneous slurry by treating with enzymes. This preparation is used to place adducts on calf thymus DNA. About 10 mg of DNA, incubated with the cells from one rat, will yield about one or two micrograms of adducted DNA. This procedure is required because of a possible need to have the cytochrome P-450 system coupled with the aryl hydrocarbon hydroxylase (AHH) enzyme system, which is responsible for the adducting of polycyclic aromatic hydrocarbons to DNA.

15. Protein Modulation Studies of Human Colon Tumor Cell Line HT-29

D.J. Reeder and J.J. Edwards

In a collaborative study with Dr. Martin Lipkin of the Memorial Sloan-Kettering Cancer Center, we have applied our capabilities for separating and quantifying small amounts (picograms) of proteins to investigating the modulation of selected proteins in human colon cancer cells. The human colon tumor cell line HT-29 has been extensively studied by researchers at Sloan-Kettering and is known to undergo, under chemical treatment, a transformation from normal pathology through a pre-cancerous state to that of a carcinoma. We received two sets of cells treated with sodium butyrate as inducing agent from Dr. Lipkin's laboratory. Each set consisted of untreated controls, treated samples taken at various time intervals up to 96 h, and a 96 h untreated control.

Cells from the 5 mM butyrate treated set and controls were chosen for initial analysis. It was assumed that each cell pellet contained 2 to 3 million cells which we solubilized by sonication in a dissolution buffer.

Electrophoretic separation by isoelectric focusing in the first dimension was performed in duplicate on all samples. The gels containing the focused proteins were then equilibrated for separation on SDS slab gels in the second dimension.

Separated proteins were visualized following silver staining. Gels from each time period were then analyzed by digital imaging on the BioImage Visage system. Image analysis included global quantification of all spots on each gel and automatic gel matching (between control and experimental samples). Information archived on a spot list for each gel included spot number, x and y coordinates, integrated intensity, area, and shape.

We found at least 14 proteins that changed significantly after being treated by the inducing agent. Four of the proteins which were not present in control cells were rapidly induced and peaked in intensity at twelve to twenty-four hours. Five other proteins, which were present in the control cells, disappeared or became very faint by twelve to twenty-four hours. Of the other proteins observed, a more gradual appearance or disappearance was noted.

Correlations of molecular weight and isoelectric point information with protein modulation are currently being made. Future investigations will focus on identification of the proteins through immunological means or by performing peptide sequencing of the N-terminal amino acids. This information will be useful in correlating the known details about the genetic makeup and gene sequences of HT-29 cells with the proteins being regulated and modulated in these experiments. This work may have an important impact in determining efficacy of cancer-modifying agents.

16. Establishment of a New Five-Year Agreement with EPA for Development of Reference Materials

W.E. May

The Environmental Monitoring Systems Laboratory of the Environmental Protection Agency at Las Vegas, (EMSL-LV) has the responsibility for providing reference materials to support EPA's hazardous waste program. Because of the nature of the problems inherent in preparation of the reference materials needed to address this mission, EPA's EMSL-LV, in 1982, established the first of two interagency agreements with NBS to provide technical advice and prepare several of the reference materials needed in this program.

During the period covered by the first five-year agreement, several reference materials were prepared and delivered to EPA EMSL-LV for their internal QA use including: PCBs in serum, organics in a liquid sludge, organics in a solid sludge, phenols and phthalates in urine, and volatile organics in whole blood.

During the past year, a new five-year agreement has been put in place which establishes a formal program for NIST to work with the EMSL-LV to develop reference materials for (1) solid and liquid wastes and (2) body fluids, with certified values for selected organic constituents. These materials will be called EPA/NIST Reference Materials and will be distributed to the entire measurement community through sales by the NIST Office of Standard Reference Materials. EMSL-LV will receive 10% of each reference material lot for their internal use. The protocols used for certification of these materials will be comparable to those used to certify NIST SRMs, and the funds recovered will be utilized to reissue these reference materials when necessary.

The first of these EPA/NIST Reference Materials will be "Cotinine in Freeze Dried Urine". Cotinine (5-3'-pyridyl)-1-methylpyrrolidone-2) is a major metabolite of nicotine that is commonly measured to determine the impact of passive exposure of non-smokers to side-stream cigarette smoke. It has a biological half-life of approximately 20 hours, is found in both the blood serum and urine of smokers, and has been shown to be linearly related to nicotine intake. This material consists of three lots of freeze-dried urine at different cotinine concentrations: (1) a blank level, containing cotinine at < 1 ppb, (2) a low level, containing cotinine at approximately 50 ppb, and (3) a high level, containing cotinine at approximately 500 ppb. The low, and high levels were prepared gravimetrically by spiking the blank urine with known quantities of cotinine perchlorate. The gravimetric values were verified by GC/MS.

17. Determination of the Catalytic Activity of Aspartate Aminotransferase (AST) Reference Material (RM 8430)

J.J. Edwards

Aspartate aminotransferase (AST) is present in most animal and plant tissues. In mammals, highest levels of AST are in liver, muscle and nerve tissue. Two distinct forms of AST exist; a soluble cytoplasmic isoenzyme and a mitochondrial isoenzyme. The cytoplasmic form is present in circulating erythrocytes and exhibits kinetic properties indistinguishable from the cytoplasmic forms found in liver and muscle. In most human pathological disturbances associated with increased AST activities in serum (e.g., acute hepatitis, hepatic malignancy, myocardial infarction) the predominant form found is cytoplasmic AST. Therefore, AST from human erythrocytes give qualitatively and quantitatively similar reactions to the isoenzymes found in normal serum and in the serum of most patients exhibiting an increased activity as a result of disease.

The work reported here was designed to measure the catalytic activity concentration of AST (AST E.C.2.6.1.1) and to provide a reference material (RM) for clinical laboratory use in evaluating and improving the precision of AST assays. The project was coordinated by members of the National Committee for Clinical Laboratory Standards (NCCLS) and by the Center for Analytical Chemistry. Two round robin exercises were conducted.

The second round-robin, in which the final activity values were determined, involved participants from seven U.S. and three European laboratories. Material for analysis was a lyophilized form of cytoplasmic AST isoenzymes obtained from human erythrocytes prepared by Dade/Baxter Travenol Inc., Miami, Florida. All cooperating laboratories used the International Federation for Clinical Chemistry (IFCC) reference method for AST to assign a numerical value for enzyme activity concentration in terms of U/L. In each laboratory, duplicate assays were performed on two vials of material on each of five days for a potential total of 200 discrete results. An analysis of variance with use of weighting factors gave a value for RM 8430 of 96.1 U/L that has an uncertainty of ± 2.6 U/L. This activity concentration and uncertainty value is equivalent to 1602 ± 43 nanokatals per liter. The reported concentration is a consensus value, i.e., the mean of results of the ten participating laboratories. The uncertainty is two standard deviations of the mean and included an allowance for observed vial-to-vial variability.

The details of this study are described in Clin. Chem. 34: 450-9 (1988). Based on the findings of this study an NBS certificate for RM 8430 has been issued.

18. Development of SRMs for Marine Pollution Monitoring

S.N. Chesler, M.M. Schantz, B.J. Koster, R.M. Parris, R.E. Rebbert, and S.A. Wise

During the past three years, the National Oceanic and Atmospheric Administration (NOAA) has supported the development of both calibration solution and natural matrix SRMs to assist in providing an accuracy base for their National Status and Trends monitoring program. Six calibration solution SRMs containing selected polycyclic aromatic hydrocarbons (PAH), chlorinated pesticides, and polychlorinated biphenyls (PCB) have been prepared and certified or are currently in progress. A marine sediment and mussel tissue material are currently being prepared and certified as natural matrix SRMs for organic contaminant measurements.

The solution-based SRMs were developed to provide accurate calibration solutions to determine chromatographic detector response factors and retention times primarily for gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS). We have prepared a series of six calibration solutions that contain selected members of the three compound classes of interest (PAH, PCB, and chlorinated pesticides) at two concentration levels: SRM 1491 Aromatic Hydrocarbons in Hexane/Toluene, SRM 1492 Chlorinated Pesticides in Hexane, SRM 1493 Polychlorinated Biphenyls in 2,2,4-Trimethylpentane, SRM 2260 Aromatic Hydrocarbons (Nominal 75 μg/g Concentration) in Toluene, SRM 2261 Chlorinated Pesticides (Nominal 3 μg/g Concentration) in Hexane, and SRM 2262 Chlorinated Biphenyls (Nominal 3 μg/g Concentration) in 2,2,4-Trimethylpentane. SRMs 1491 and 2260 contain 24 analytes; SRMs 1492 and 2261 contain 15 analytes; and SRMs 1493 and 2262 contain 20 and 28 PCB congeners, respectively. SRMs 2260, 2261, and 2262 were requested by NOAA and EPA to provide more concentrated solutions that could be diluted to prepare multipoint calibration curves for quantitation. In addition, the higher levels of the chlorinated pesticides and PCBs in SRMs 2261 and 2262 are sufficient to allow quantitation by GC/MS and GC-flame ionization detection (FID) rather than the more sensitive GC with electron capture detection (ECD). Eight additional congeners, which were recommended by EPA, were included in SRM 2262 for use in determining response factors for GC as specified in EPA Method 680. Certification of all the calibration SRMs was based on GC and gravimetric measurements.

For the development of SRM 1941 Organics in Marine Sediment, a large quantity of sediment was collected in Baltimore Harbor with the assistance of a NOAA contractor. This material was air dried, ground, sieved, homogenized, and bottled in 60-g aliquots as the SRM. Measurements for the determination of PAH, by GC-FID and LC with fluorescence detection, have been completed with good agreement between the two techniques. About 10-12 PAH will be certified with concentrations ranging from about 200 ng/g for anthracene to 1000-1100 ng/g for fluoranthene and pyrene. Selected PCB congeners and chlorinated pesticides have been determined by GC-ECD and additional measurements by multidimensional GC will be made in FY-89. Trace element analyses have been performed by neutron activation analysis to provide noncertified information values.

The second SRM under development for use in monitoring marine pollution is SRM 1974, Organics in Mussel Tissue (Mytilus edulis). Approximately 3000 mussels were collected at two sites near Boston, MA: Dorchester Bay in Boston Harbor and Buzzards Bay near New Bedford, MA. Aliquots of samples from the two sites were homogenized and analyzed to determine the suitability of the materials as the proposed SRM. After analysis of the samples by GC-MS, it was determined that the Dorchester Bay material had suitable levels of the analytes of interest: PAH (e.g., fluoranthene and pyrene at 200 ng/g dry weight), PCBs (10-50 ng/g dry weight for individual PCB congeners), and chlorinated pesticides (10-20 ng/g dry weight for 4,4′-DDE, 4,4′-DDT, and 4,4′-DDD). The 28 kg of material from Dorchester Bay will be cryogenically homogenized and distributed frozen in 15-g aliquots as SRM 1974. SRM 1974 will be the first tissue SRM issued specifically for the determination of organic constituents and the first tissue to be issued as a fresh frozen material rather than a dried material. SRM 1974 will have certified concentrations for selected PAH, PCB congeners, and chlorinated pesticides. Homogenization and mixing of this material are currently in progress and analytical measurements (LC/fluorescence and GC-MS for PAH; GC-ECD and multidimensional GC-ECD for the PCB and pesticides) will commence at the beginning of FY-89.

19. Development of SRM 1597, Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar

S.A. Wise, B.A. Benner, G.D. Byrd, R.E. Rebbert, and M.M. Schantz

Since 1933 when several polycyclic aromatic hydrocarbons (PAH) were isolated from coal tar and found to be highly carcinogenic, PAH have been one of the most widely measured groups of environmental pollutants. To assist in validating the accuracy of PAH measurements, several Standard Reference Materials (SRMs) have been issued by the National Bureau of Standards since 1980 for use in the determination of these compounds. These SRMs range in analytical difficulty from a simple calibration solution of the 16 priority pollutant PAH (SRM 1647) to several complex, natural matrix materials such as shale oil (SRM 1580), crude oil (SRM 1582), air particulate material (SRM 1649), and diesel particulate matter (SRM 1650). A new SRM, which is intermediate in complexity when compared to existing SRMs, has been prepared and certified for use in the determination of PAH. SRM 1597 Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar consists of a natural mixture of PAH isolated from a crude coke-oven tar and dissolved in toluene. This complex combustion-related PAH mixture is suitable for direct analysis (i.e., without sample cleanup or concentration) using such techniques as liquid chromatography (LC), gas chromatography (GC), or gas chromatography-mass spectrometry (GC-MS).

For quantitation of the compounds in SRM 1597, GC with flame ionization detection and LC with fluorescence detection were used as the two independent analytical techniques. Certified concentrations are reported for 12 PAH, and concentrations for an additional 18 compounds are reported as informational values. SRM 1597 has the largest number of certified and informational values for PAH of any of the natural matrix SRMs. For the majority of the compounds measured, both the GC and LC analyses were performed without concentration or cleanup of the sample (i.e., direct analysis). Using a direct analysis LC method made it impossible to obtain accurate data for triphenylene or benzo[ghi]perylene because of low detection sensitivity or selectivity. To obtain LC data for these two compounds, a normal-phase LC fractionation procedure was employed to isolate separate fractions containing these components which were suitable for reversed-phase LC analysis. Chrysene and triphenylene are not routinely quantified by GC analyses since they coelute on conventional nonpolar stationary phases. To provide the necessary data from a second technique for certification, these two isomeric PAH were determined by GC analysis on a liquid crystalline stationary phase. SRM 1597 is the first SRM with certified concentrations for chrysene and triphenylene.

Approximately 60 compounds were identified in SRM 1597 based on molecular weight information from GC-MS analysis and on the comparison of GC retention data with reference standards and literature data. GC retention indices were determined for a number of the compounds in this material and are compared with literature data on the Certificate of Analysis. In addition to the PAH, SRM 1597 contains numerous other polycyclic aromatic compounds as minor components, including sulfur heterocycles, nitrogen heterocycles, and oxygen heterocycles. PAH mixtures from coal tar have already found use in a number of laboratories for the evaluation of gas chromatographic performance (e.g., column efficiency and/or selectivity). Therefore, SRM 1597 will serve as a common reference sample for such comparisons among laboratories. The preparation and certification of this SRM have been described recently in **Anal. Chem. 60**:887-894 (1988).

20. Development of SRMs for Cholesterol in Human Serum

P.M. Ellerbe, L.T. Sniegoski, M.J. Welch, and E. White V

Large epidemiological studies have shown a direct link between the level of cholesterol in a person's blood and their risk of coronary heart disease. Since heart disease is the number one cause of mortality in the United States, a major effort is underway to make people aware of the importance of knowing their blood cholesterol levels and taking appropriate action if the level is too high.

The accurate measurement of cholesterol levels in serum is a matter of public concern. Proficiency testing programs have shown wide discrepancies in cholesterol results among clinical laboratories and among the commonly used methods. Reference materials with accurately determined concentrations of cholesterol in appropriate matrices are an important component in assessing the quality of measurements in clinical laboratories. In cooperation with the College of American Pathologists and the Centers for Disease Control, NIST has developed such a series of Standard Reference Materials (SRMs) for human serum.

Two new serum-based SRMs have been certified for total cholesterol in the past year. One of these (SRM 1951) consists of three levels (210, 242, and 282 mg/dL) in a frozen serum matrix. The other (SRM 1952) consists of three levels (207, 262, and 357 mg/dL) in a freeze-dried serum matrix. Because of the demand for these SRMs, 1952 sold out within a few months and 1951 is selling rapidly. A replacement material, SRM 1952a, consisting of three levels in a freeze-dried serum, is now being certified. Certification is also underway for SRM 909a, a replacement material for SRM 909, a freeze-dried serum certified for a large number of organic and inorganic analytes. This new material will have two levels of all of these analytes. The certification measurements for total serum cholesterol are made using the isotope dilution mass spectrometric definitive method. This method has been carefully and thoroughly tested for sources of bias and imprecision, and found to exceed the guidelines for accuracy and precision recommended for definitive methods. Briefly, the method involves the following steps: (1) A known weight of cholesterol-$^{13}C_3$ is added to a known weight of serum; (2) the serum is subjected to alkaline hydrolysis to free cholesterol from its esters; (3) the cholesterol, both labeled and unlabeled, is extracted and converted to a trimethylsilyl derivative; (4) the derivatized material is injected into a GC/MS system equipped with a fused silica capillary column with a nonpolar bonded phase; (5) the mass spectrometer is set to monitor the intensities of the molecular ions for the unlabeled and labeled cholesterol derivative; (6) standard mixtures consisting of known amounts of pure unlabeled cholesterol (SRM 911a) and cholesterol-$^{13}C_3$ are measured immediately before and after each sample to bracket the sample in both ratio and time. Each sample is measured twice with the order of bracketing standards reversed. A subset of each group of samples is remeasured using different ions and/or different chromatographic conditions as a test for bias in the original measurements. Because of the soundness of the procedure and the careful attention to detail in the sample preparation and measurements, we routinely achieve results with relative standard deviations of <0.4% and no evidence for systematic bias.

The availability of such matrix reference materials with accurately determined analyte concentrations provides a means for evaluating and improving the accuracy of field methods used in clinical laboratories.

21. Development of SRMs for Drugs of Abuse in Urine

G.D. Byrd, N.E. Craft, R. Espinosa-Leniz, L.R. Hilpert, S. Tai, and M.J. Welch

Substance abuse is a major concern in the United States. The number of organizations, both public and private, which require drug testing for employees and job applicants is rapidly growing. The repercussions of a positive test for drugs of abuse can be enormous, thus it is imperative that drug testing be highly accurate. It is generally recognized that screening tests cannot be considered positive unless they are confirmed by gas chromatography/mass spectrometry (GC/MS). GC/MS can generally provide unambiguous identification of drugs of abuse in urine samples and can, with proper procedures, provide accurate quantitation of the amount present. One major component in quality assurance for drug testing programs is the use of reference materials to demonstrate that methods are being properly run.

We are involved in a program to develop and certify urine-based Standard Reference Materials for drugs of abuse. The first of these materials, SRM 1507, consists of two vials of freeze-dried urine with approximately 20 ng/mL (when reconstituted) of 11-nor-delta-9-tetrahydrocannabinol-9-carboxylic acid (THC-9-COOH), the primary urinary metabolite of the psychoactive component of marijuana. The SRM also includes a vial of a blank urine. Certification of this material was recently completed and involved the use of a GC/MS method and an HPLC method.

The GC/MS method used for certification involved spiking a 10-mL aliquot of the reconstituted urine with a deuterated analog of the metabolite, isolating the analyte and internal standard with a solid phase extractor, converting them to the trimethylsilyl (TMS) derivatives, and injecting the derivatized sample into the GC/MS system for measurement. The GC was equipped with a 30-meter fused silica capillary column with a non-polar bonded phase. The mass spectrometer was a single quadrupole instrument operated in the electron impact mode at 70 eV with an ion source temperature of 200 °C. The molecular ions at m/z 488 and 491 were monitored. Response factor solutions consisting of known amounts of the analyte and internal standard (as the TMS derivatives) were run frequently for calibration. A total of 24 vials (one randomly selected from each tray of vials produced) were analyzed in duplicate, yielding a concentration for the analyte of 19.9 ± 0.6 ng/mL.

The HPLC method involved spiking a 10-mL aliquot of the reconstituted urine with the 11-hydroxy isomer of the analyte, extracting the analyte and internal standard with 3% isobutanol in hexane, evaporating this phase, and dissolving the residue in methanol. The samples were analyzed by reversed-phase HPLC with a monomeric C_{18} analytical column and a mobile phase gradient. An electrochemical detector operated in the oxidative mode at +1.0 V vs. the AgCl reference electrode was used for measurement. A total of 10 aliquots from 6 vials were analyzed, yielding a concentration of 19.7 ± 0.4 ng/mL. Based upon the GC/MS and HPLC results, and an allowance for possible systematic error, the certified concentration for this SRM is 20 ± 1 ng/mL. The blank urine contained less than 1 ng/mL of THC-9-COOH.

Certification measurements are now in progress for the second SRM in this program. This material consists of three levels each of cocaine and two of its urinary metabolites, benzoylecgonine and methylecgonine plus a blank urine. This freeze-dried material is being developed in cooperation with the College of American Pathologists (CAP), who will use part of the lot in their accreditation program for laboratories engaged in testing for drugs of abuse. As with the marijuana metabolite, the certification process involves two independent methods, isotope dilution GC/MS and HPLC for both cocaine and benzoylecgonine. Because of difficulties in obtaining and analyzing pure samples of methylecgonine, this analyte will not be certified at this time, but its gravimetric value will be provided as an information value.

Future plans include more cooperative projects with the CAP to develop reference materials for drugs of abuse. The next analyte for both organizations will probably be phencyclidine (PCP).

22. The Expanded Role of the NIST Specimen Banking Program

S.A. Wise, B.J. Koster, R.M. Parris, M.M. Schantz, S.F. Stone, and R.L. Zeisler

In 1979 the Center for Analytical Chemistry (CAC), in conjunction with the U.S. Environmental Protection Agency (EPA), established a Pilot Environmental Specimen Bank Program to determine the feasibility of long-term storage of environmental samples. Human liver specimens were selected as the first sample type to be included in this pilot program. Over 550 liver specimens have been collected and stored in the specimen bank facility since 1980. In recent years, interest in the concept of environmental specimen banking, i.e., the archiving of biological specimens for retrospective analysis, has increased as such activities have been recognized as an important complement to traditional environmental pollution monitoring programs. As a result of this increasing interest, specimen banking activities at NIST have expanded beyond the original pilot effort to include a variety of specimens.

For the past three years, the National Oceanic and Atmospheric Administration (NOAA) has sponsored the banking and analysis of marine samples from their National Status and Trends Program. These marine specimens include mussels and oysters, sediment, fish muscle, and fish liver. In 1987, we initiated a project with the Alaska Office of NOAA to archive tissues from Alaskan marine mammals such as seals, walrus, and whales. During 1987 and 1988, specimens of blubber, liver, and kidney from two different species of seals (Northern fur seals and ringed seals) were collected on the Pribilof Islands and at Point Barrow, Alaska.

Two additional programs within CAC also have minor specimen banking activities associated with them. As part of the quality assurance program for the National Cancer Institute's (NCI) Micronutrient Measurement Program, human serum samples have been banked to evaluate the long-term storage stability of micronutrients (e.g., vitamins and trace elements) in these specimens. Finally, as part of a joint effort with the Food and Drug Administration (FDA), U.S. Department of Agriculture (USDA), and the International Atomic Energy Agency (IAEA), we are investigating the stability of human diet samples stored in the bank. These four projects, combined with the original EPA Pilot Environmental Specimen Bank project, now make up the National Biomonitoring Specimen Bank. The different projects have allowed NIST to gain experience in sample collection, processing, long-term sample stability under various storage conditions, analysis, and quality assurance for a variety of specimen types. As part of the development of specimen collection protocols, NIST scientists have assisted in the field during sample collection to implement and modify the sampling procedures as required for the specific circumstances.

Approximately 20% of the archived specimens in each of these projects are homogenized and analyzed to provide accurate baseline concentrations for selected trace elements and organic constituents. These baseline data are used for sample stability studies, for comparison with similar data from other laboratories, and for long-term trend monitoring. Analytical data for selected trace elements and organic contaminants (e.g., chlorinated pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons) are available on about 100 human liver specimens; fish tissue, mussels, oysters, and sediment from about 20 U.S. coastal sites; and selected seal tissues.

As a result of these increasing specimen banking-related activities, the NIST specimen bank facility is currently being expanded and upgraded. The addition to the specimen bank facility will increase the current storage capacity by a factor of three, thereby allowing the National Biomonitoring Specimen Bank to continue to serve as a resource for national monitoring programs.

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Brown-Thomas, J.M., "Careers for Women in Science," Takoma Park Intermediate School, Silver Spring, MD, November 19, 1987.

Brown-Thomas, J.M., "Chromatography," Westland Intermediate School, Bethesda, MD, January 13, 1988.

Brown-Thomas, J.M., "Science," Glen Haven Elementary School, Silver Spring, MD, February 2, 1988.

Brown-Thomas, J.M., "Chromatography," Blair High School, Silver Spring, MD, April 18, 1988.

Brown-Thomas, J.M., "What is a Chemist?," St. John School, Columbia, MD, May 27, 1988.

Brown-Thomas, J.M., "Stability of Fat-Soluble Vitamins in Human Serum as Determined by High Performance Liquid Chromatography," 102nd Annual International Meeting of the Association of Official Analytical Chemists, Palm Beach, FL, August 30, 1988.

Christensen, R.G., "Determining the Purity of 'Pure' Materials," Indiana University of Pennsylvania, Chemistry Department, Indiana, PA, February 5, 1988.

Coxon, B., "Two-Dimensional NMR Spectrum Editing of Carbohydrates," The 195th American Chemical Society Meeting and The Third Chemical Congress of North America, Toronto, Canada, June 8, 1988.

Craft, N.E., "HPLC-EC Determination of 11-Nor-Delta-9-Tetrahydrocannabinol-9-Carboxylic Acid in SRM 1507: 11-Nor-Delta-9-THC-9-Carboxylic Acid in Lyophilized Urine," Annual Meeting of Federation of American Societies for Experimental Biology, Las Vegas, NV, May 5, 1988.

Durst, R.A., "Liposome-Enhanced Flow Injection Immunoanalysis System," University of Houston, Department of Chemistry, Houston, TX, January 16, 1988.

Durst, R.A., "Liposome-Enhanced Flow Injection Immunoanalysis," The Oak Ridge Conference on Advanced Analytical Concepts for the Clinical Laboratory, Savannah, GA, April 14, 1988.

Durst, R.A., "Dual-Function Polymer-Modified Electrode for the Measurement of Liposome-Released Ferrocyanide," The 195th., Toronto, Canada, June 7, 1988.

Edwards, J.J., "Separation and Characterization of Fibronectic Domains by Two-Dimensional Gel Electrophoresis," Electrophoresis Society, Charleston, SC, June 15, 1988.

Espinosa-Leniz, R., "A Solid Phase Extraction Method for GC/MS Analysis of Cocaine and its Major Metabolites in Urine," American Society for Mass Spectrometry, Annual Meeting, San Francisco, CA, June 9, 1988.

Guenther, F.R., "Residential Wood Combustion: A Source of Atmospheric Polycyclic Aromatic Hydrocarbons," Ninth International Symposium on Capillary Chromatography, Monterey, CA, May 19, 1988.

Koster, B.J., "Technical Improvements in the Operation of the U.S. National Biomonitoring Specimen Bank Facility," 11th U.S.-German Seminar of State and Planning for Environmental Specimen Banking, Bayreuth, Bavaria, Federal Republic of Germany, May 3, 1988.

Margolis, S.A., "Stabilization of Ascorbic Acid in Serum and Its Measurement by HPLC," Annual Meetings of Federation of American Societies for Experimental Biology, Las Vegas, NV, May 5, 1988.

Margolis, S.A., "Structure of Thymine-Tyrosine Dimer," 14th International Congress of Biochemistry, Prague, Czechoslovakia, July 15, 1988.

May, W.E., "Development of SRMs for Environmental Trace Organic Analysis," First International Symposium on Trace Analysis in Environmental Samples and SRMs, Honolulu, HI, January 6, 1988.

May, W.E., "The Aqueous Solubility Behavior of Polycyclic Aromatic Hydrocarbons," University of Maryland, College Park, MD, February 4, 1988.

May, W.E., "NIST: What is it?? Where is it?? and What do they do??," Alabama A&M University, Chemistry Department, Huntsville, AL, February 5, 1988.

May, W.E., "Reference Materials for Drugs of Abuse in Urine," Pittsburgh Conference & Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, February 25, 1988.

May, W.E., "Fundamental and Applied Research Activities in Liquid Chromatography at the National Bureau of Standards," 15th Annual National Conference, National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Philadelphia, PA, April 5, 1988.

May, W.E., "Reflections on the Arthur S. Flemming Award from a Recent Recipient," Fortieth Annual Arthur S. Flemming Awards Program, Washington, DC, May 6, 1988.

May, W.E., "Development of a Marijuana in Urine SRM," University of Maryland, College Park, MD, May 6, 1988.

May, W.E., "Role of the NBS Center for Analytical Chemistry in Assuring the Quality of Chemical Measurements in the U.S.," Ohio Valley Chromatography Symposium, Miami University, Oxford, OH, June 15, 1988.

May, W.E., "International Collaborative Study to Evaluate Bioassay Methods," NESCAUM, Symposium on the Use of Biological Tests in Evaluation of Ambient Air Pollutants: Implications for Regulatory Agencies, Princeton, NJ, September 14, 1988.

Parris, R.M., "Standard Reference Materials for Organic Environmental Analysis," Workshop on Environmental Analysis-RCRA Methods, ACS, NBS, CMA, Water Pollution Control Federation, National Bureau of Standards, Gaithersburg, MD, October 3, 1987.

Parris, R.M., "Organic Analysis of Banked Human Liver Specimens to Determine Storage Stability," 11th U.S.-German Seminar of State and Planning for Environmental Specimen Banking, Bayreuth, Bavaria, Federal Republic of Germany, May 2, 1988.

Parris, R.M., "NBS Standard Reference Materials for the Determination of Chlorinated Biphenyls, Chlorinated Pesticide, and Other Halogenated Compounds," 3rd International Symposium on Biological Reference Materials, Bayreuth, Bavaria. Federal Republic of Germany, May 5, 1988.

Plant, A.L., "Biosensors," Biotechnology Lunch Group, Gaithersburg, MD, November 4, 1987.

Plant, A.L., "Current Research in Flowing Immunoassay Development," IGEN Corporation, Rockville, MD, November 9, 1987.

Plant, A.L., "Flow Injection Analysis and Biosensors," Environmental Protection Agency, Cincinnati, OH, December 2, 1987.

Plant, A.L., "Liposomes as Immunoreagents," Chemistry Club, University of Maryland, Baltimore, MD, April 13, 1988.

Plant, A.L., "Flow Injection Immunoassay," Gordon Research Conference on Bioanalytical Sensors, New London, NH, June 17, 1988.

Reeder, D.J., "Electrophoresis in Bioanalytical Setting," NIH Meeting Sponsored by Eastman Kodak & Subsidiaries, Bethesda, MD, February 17, 1988.

Reeder, D.J., "Electrophoresis Standards and their Development," Harvard Medical School, Boston, MA, February 22, 1988.

Reeder, D.J., "Electrophoresis and Bioanalytical Research at NBS," University of Utah Center for Biopolymers at Interfaces, Salt Lake City, UT, March 10, 1988.

Reeder, D.J., "Electrophoretic Principles and Standards," Rockfeller University, New York, NY, May 19, 1988.

Reeder, D.J., "Analysis of Proteolytic Digestion of Fibronectin by Computerized Image Processing of Two-Dimensional Gels," Electrophoresis Society, Charleston, SC, June 14, 1988.

Richie, K.L., "Results of an Interlaboratory Study to Assess Reproducibility of Rehydratable Gels," Electrophoresis Society, Charleston, SC, June 16, 1988.

Sander, L.C., "Evaluation of Column Performance for Reversed Phase Liquid Chromatography," Pittsburgh Conference & Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, February 23, 1988.

Sniegoski, L.T., "Determination of Cholesterol in Human Serum Standard Reference Materials by Isotope Dilution /Mass Spectrometry," Third International Symposium on the Synthesis and Applications of Isotopically Labelled Compounds, Innsbruck, Austria, July 18, 1988.

Sundaram, P., "The Past, Present and Future of Biosensors," IX Enzyme Engineering Conference, Santa Barbara, CA, October 4, 1987.

Welch, M.J., "The Development of Definitive Methods for Organic Serum Constituents," University of Maryland, Department of Chemistry, University of Maryland, College Park, MD, December 4, 1987.

Welch, M.J., "How Pure is Pure? The Certification of Cholesterol 911b," American Society for Mass Spectrometry, Annual Meeting, San Francisco, CA, June 8, 1988.

Welch, M.J., "Criteria for Cholesterol Reference Materials," American Association for Clinical Chemistry, Annual Meeting, New Orleans, LA, July 24, 1988.

Wise, S.A., "The U.S. National Biomonitoring Specimen Bank - Summary of Recent Activities," 11th U.S.-German Seminar of State and Planning for Environmental Specimen Banking, Bayreuth, Bavaria, Federal Republic of Germany, May 1, 1988.

Wise, S.A., "Organic Analysis of Marine Specimens from the National Oceanic and Atmospheric Administration's National Status and Trends Program," 11th U.S.-German Seminar of State and planning for Environmental Specimen Banking, Bayreuth, Bavaria, Federal Republic of Germany, May 2, 1988.

Wise, S.A., "Standard Reference Materials for the Determination of Polycyclic Aromatic Hydrocarbons," 3rd International Symposium on Biological Reference Materials, Bayreuth, Bavaria, Federal Republic of Germany, May 5, 1988.

Wise, S.A., "Selectivity in Reversed-Phase Liquid Chromatography," Department of Analytical Chemistry, University of Ulm, Federal Republic of Germany, May 10, 1988.

Wise, S.A., "Shape Selectivity in Liquid and Gas Chromatography: Polymeric Octadecylsilane (C_{18}) and Liquid Crystalline Stationary Phases," The 195th Annual American Chemical Society Meeting and The Third Chemical Congress of North America, Toronto, Canada, June 7, 1988.

Wise, S.A., "Experience in Environmental Specimen Banking," 18th International Symposium on Environmental Analytical Chemistry, Barcelona, Spain, September 5-8, 1988.

Wise, S.A., "Reference Materials for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Samples," University of Bordeaux, Bordeaux, France, September 12, 1988.

3. Committee Assignments

Willie E. May

ACS Environmental Chemistry Division
ACS Education Committee
Coordinating Research Council-Air Pollution Research Advisory Board
Special Topics Sub-Committee Chairman, International Committee on Polycyclic Aromatic Hydrocarbons
Board of Governors, International PAH Symposium
USDA/FDA/NIST Food Irradiation Research Steering Committee

Bruce Coxon

ASTM E-13 on Molecular Spectroscopy
Secretary, ASTM Subcommittee E-13.07 on Nuclear Magnetic Resonance

Richard A. Durst

ASTM D-19 on Water
ASTM E-48 on Biotechnology; Chairman, Subcommittee on Biosensors
Board of Advisory Editors, Selective Electrode Reviews
Secretary, IUPAC Division V on Analytical Chemistry; Commission 5 on Electroanalytical Chemistry
Advisor, NCCLS Subcommittee on Electrolytes
NCCLS Subcommittee on pH and Blood Gases
Chairman, NCCLS Area Committee on Instrument Systems
Chairman, NIST Colloquium Committee
Board of Directors, Society for Electroanalytical Chemistry

Jesse J. Edwards

ASTM E-48 on Biotechnology

Diane K. Hancock

Referee, U.S. National Committee on Sugar Analysis, Subcommittee 6 on Quartz Control Plates
Associate Referee, International Commission for Uniform Methods of Sugar Analysis

Dennis J. Reeder

AACC Committee on Standards; Study Group on Total Serum Protein
Associate Member, IFCC Expert Panel on Drug Effects in Clinical Chemistry
NCCLS Subcommittee on Total Protein
Vice President, International Electrophoresis Society

Michael J. Welch

Standards Committee of the American Association for Clinical Chemistry

Stephen A. Wise

President, Washington Chromatography Discussion Group (1987-1988)

Co-Chairman, Sub-Committee on Chromatography, International Committee on Polycyclic Aromatic Hydrocarbons

Chairman, Publicity Committee, Division of Analytical Chemistry, American Chemical Society

4. Other

a. Seminars

October 8, 1987

Mr. Michael Zeece, Dept. of Food Science, Univer
"**Two-Dimensional Electrophoresis of Wheat Proteins**" (Division Sponsor: Dennis J. Reeder)

November 30, 1987

Prof. Karl M. Kadish, Department of Chemistry, University of Houston, Talk entitled: "**The Chemistry and Electrochemistry of Metalloporphyrins**" (Division Sponsor: Richard A. Durst)

January 7, 1988

Dr. G. Russell Warnick, Northwest Lipid Research Clinic, Seattle, WA, Talk entitled: "**Cholesterol Measurements in the Clinical Laboratory**". (Division Sponsor: Robert Schaffer)

June 27, 1988

Ms. Kathryn S. Kalasinsky, Mississippi State University, Talk entitled: "**Chromatographic Infrared Techniques and Applications in Analytical Chemistry**" (Division Sponsor: Willie E. May)

b. Conferences Sponsored

December 7 & 8

NOAA/NBS Quality Assurance Workshop, NBS, Gaithersburg, MD, Stephen N. Chesler.

Sept. 30 - Oct. 2

NBS/NCI Micronutrient Analysis Workshop, NBS, Gaithersburg, MD, Willie E. May.

June 13 - 17

Gordon Research Conference on Bioanalytical Sensors, Colby-Sawyer College, New London, NH, Richard A. Durst.

c. SRM Activities

Certification:

SRM 909a, Human Serum
SRM 911b, Cholesterol (crystalline)
SRM 914a, Creatinine (crystalline)
SRM 916a, Bilirubin (crystalline)
SRM 1216, Carbon Modified Silica
SRM 1491, Polycyclic Aromatic Hydrocarbons in Hexane/Toluene
SRM 1492, Pesticides in Hexane
SRM 1493, PCB Congeners in Iso-Octane

SRM 1507, THC in Freeze Dried Urine
SRM 1563, Cholesterol and Fat-Soluble Vitamins in Coconut Oil (Natural and Fortified)
SRM 1588, Organics in Cod Liver Oil
SRM 1597, Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar
SRM 1647a, Polycyclic Aromatic Hydrocarbons in Acetonitrile
SRM 1941, Marine Sediment/Organics
SRM 1951, Cholesterol in Human Serum (Frozen)
SRM 1952, Cholesterol in Human Serum (Freeze-Dried)
SRM 1952a, Cholesterol in Human Serum (Freeze-Dried)
SRM 8430, Aspartate (AST) Aminotransferase in 3% Albumin Solution

Stability Measurements:

SRM 909, Human Serum
SRM 1614, Dioxin in Iso-Octane
SRM 1649, Urban Dust/Organics
SRM 1650, Diesel Particulate Matter

IV. Gas and Particulate Science Division

Rance A. Velapoldi, Chief

A. Division Overview

The Gas and Particulate Science Division conducts research to develop new and improved techniques for the preparation and analysis of gas mixtures and macroscopic and microscopic regions of condensed phase materials. This includes research leading to: (a) improved measurements of gaseous species in the atmosphere and in specially prepared gas mixtures and standards, (b) new chemometric techniques for improving the chemical measurement process and determining source apportionment, (c) improved methods for quantitative electron, ion, and photon microanalysis, and (e) the preparation and certification of reference materials, including SRMs, for measurement quality assurance in analytical chemistry. The Division responds to the measurement and standards needs of other Federal agencies, state and local governments, industrial organizations, and universities.

The year 1988 was very satisfying and productive for the Division Staff in terms of funding and scientific accomplishments. Although competence funding was discontinued at the 5-year 'sunset' limit in the now mature area of elemental compositional mapping, the Microanalysis Group was successful in competitive presentations and obtained new competence funding for molecular compositional mapping, an area using principles similar to elemental mapping, but generally using different instrumentation to obtain molecular species information.

The efforts of the Division have supported the basic NIST mission to serve emerging technologies as well as existing technologies by developing new measurement techniques, extending existing techniques to new matrices, analytes, and lower concentrations, making more accurate measurements, and developing and certifying materials as SRMs. This year has been no exception, with major efforts in all of these areas.

The breakthroughs and refinements made earlier by the Atmospheric Chemistry Group to apply accelerator mass spectrometric measurements to microgram quantities of ^{14}C obtained from gases have been followed by extending these ^{14}C measurement techniques to amino acids obtained from fossilized bones and to organic species such as polynuclear aromatic hydrocarbons obtained from geologic samples. These two major advances open vast new measurement areas for microchemical and molecular dating and to source apportionment. Additionally, definitive treatises on detection limits and the chemical measurement process have been published; both of these major works set the standards in, and advance, the field of analytical chemistry.

After obtaining support of NIST CO_2 SRMs at the World Meteorological Organization's (WMO) annual meeting, the Gas Metrology Group continued work on these standards and obtained a decrease in the measurement uncertainty by a factor of more than 3, reducing the uncertainty at the 95% level from about 0.9 ppm to about 0.3 ppm over the concentration range of 300 to 410 ppm CO_2. Additionally, an isotope dilution mass spectrometric definitive measurement method was developed for determining atmospheric CO_2. These IDMS measurements gave results that agreed with the SRM CO_2 concentrations within 0.2 ppm over the 300 to 375 ppm range, providing excellent agreement with the gravimetric values, as well as providing an extremely firm foundation to tie all global CO_2 monitoring results to CO_2 standards based on accurate measurements.

To increase NIST leverage in the production and use of SRMs, the Gas Metrology Group has also signed a two-year agreement with the Motor Vehicle Manufacturers' Association which, working in conjunction with a MVMA Research Associate (William Thorn), should provide seven new gas standards and renewal of four others. These standards are used to calibrate instrumentation in the automotive manufacturers' laboratories that determine adherence to automobile emission laws.

As reported last year, Congress mandated the Asbestos Hazard Emergency Response Act of 1986 (AHERA) and the Division was given major responsibility to provide the technical support for accrediting laboratories conducting bulk and airborne asbestos measurements by polarized light microscopy (PLM) and analytical transmission electron microscopy (ATEM), respectively. This first year the asbestos team, headed by Eric Steel in the Microanalysis Research Group, performed extraordinarily well, providing measurement methods, technical accreditation criteria, SRMs, and audit materials for bulk asbestos measurements. These were presented to private testing laboratories, Federal, state, and local agencies, and the public during the extremely successful Johnson Conference held in Vermont during July. Detailed discussions, and acceptance of the criteria and methods took place at the Johnson Conference where the measurement method for bulk asbestos was being submitted concurrently through the ASTM review process. The Division staff worked closely with the National Voluntary Laboratory Accreditation Program (NAVLAP) staff at NIST to address all facets of the laboratory accreditation program including developing the criteria, and selecting and training the more than 60 auditors who will visit the laboratories desiring accreditation. The focus this year will be on developing a similar program for the airborne asbestos measurements using the ATEM, as well as continuing with the laboratory accreditation program for bulk asbestos measurement.

During the past year, the Microanalysis Research Group built an electron/x-ray optical bench to measure more accurately fundamental x-ray parameters critical in quantitative chemical analysis using electron probes on a microscale. The bench offers flexible control of the electron beam, specimen, and detection. This versatility provides us with the ability to make more accurate measurements of the fundamental x-ray parameters used in the quantitative analysis of thin films, particles, and specimens containing light elements such as oxygen, as well as research on the use of low energy electron beams for quantitative analysis. Preliminary measurements on the absorption of x-rays as a function of emergence angle have been made and compared to existing literature expressions for absorption.

The success of using synchrotron radiation in the total reflection geometry to provide sensitive, quantitative x-ray measurements for Se in serum was reported last year and published in Analytical Chemistry in April of this year. Continued efforts to obtain more sensitivity using XRF measurements focussed this year on two major themes: the development of chelation exchange membranes for element preconcentration and the use of total reflection geometry combined with a rotating anode x-ray source. Experiments in the former are promising; however, increased membrane capacity and reproducibility have to be attained to provide a reliable, accurate, quantitative measurement procedure. In the latter, components of the rotating source instrument (double crystal spectrometer, capability for orienting detector/sample combinations, reduced pressure/He path operation) have been purchased or designed, built, and assembled. Preliminary measurements have been used to characterize the topography of metallurgical surfaces and efforts this year will focus on determining minimum detection limits (mdl) for selected elements for comparison with those mdl's determined using the synchrotron technique.

The Gas Metrology and X-Ray Fluorescence Groups have continued their strong efforts this year in SRM certification. More than 150 SRMs have been measured, certified, and/or recertified, ranging from gases useful in studying atmospheric constituents and phenomena such as the greenhouse effect and ozone layer depletion to establishing homogeneity for broadly-used biological SRMs including orchard and peach leaves.

Increased research capability continues to be a critical need and challenge in specific areas of the Division. With the asbestos group firmly established, the focus this year will be on strengthening gas measurement research, chemometrics, and molecular microprobe research.

1. Atmospheric Chemistry Group: Overview

The program of the Atmospheric Chemistry Group has two primary objectives: (1) the development and application of advanced measurement techniques and standards to increase our knowledge for control of trace atmospheric gases and particles; and (2) the investigation of mathematical and statistical methods with application to contemporary analytical problems involving multivariable and multicomponent systems for the assessment and control of analytical accuracy. Atmospheric gases receiving primary emphasis include ozone, methane, and carbon monoxide. Particle research is directed toward experimental and mathematical methods for apportioning sources of natural and anthropogenic carbonaceous particles. In this effort, and in cooperation with the Organic Analytical Research Division and the accelerator laboratory at the University of Arizona, our laboratory has become a recognized leader in the art of ^{14}C - microorganic chemistry. Current activities in chemometrics have been directed at building a software base for the chemometrics program, developing and applying a basic strategy for sample selection for chemical analysis, and investigating "errors-in-variables" as applied to the evaluation of analytical data.

The Group continues to provide the benchmark for ambient measurements of ozone, through calibration services plus the production of ozone Standard Reference Photometers (SRP's). During the past year, three SRP's were manufactured: one for inclusion in the EPA ozone monitoring network, one for the Canadian Atmospheric Environment Service, and one for the National Swedish Environment Protection Board. These last two will provide links between the U.S. ozone measurement system and those in use in Canada and Europe. Complementing work on standard reference photometry has been the development of a stable ozone generator. The first working prototype was developed during FY88; its stability over the short term (8 hours) is better than 1%.

Particulate ^{14}C measurements performed in connection with the EPA's Integrated Air Cancer Project (IACP) have proven most valuable in providing reliable information on the apportionment of atmospheric carbon compounds and mutagenicity. The "direct" ^{14}C tracer technique, which is based on the known differences in isotopic composition of wood and fossil fuel, has also permitted us to assess the limits of validity of the EPA-proposed "indirect" elemental K, Pb tracer model. Knowledge of these limits has considerable impact on the cost and accuracy of (1) future routine monitoring for woodburning pollutant and mutagen burdens and (2) regional and global assessments of biomass burning contributions to carbonaceous particles.

The emergence of "^{14}C microorganic chemistry" has been made possible through the linkage of contamination-free, μg-level isolation of organic species to state-of-the-art accelerator mass spectrometry (AMS). The extreme sensitivity of AMS, combined with advances in target preparation in our laboratory (through the efforts of two NRC postdoctoral fellows), has made possible reliable measurements of ^{14}C in tens of μg's of selected organic species. This, in turn, has led to new insights into the origins of organic carbon in the atmosphere, as well as ages of archeological artifacts. Knowledge concerning atmospheric organic carbon was developed during the past year through (1) cooperative research with the Organic Analytical Research Division (S. Wise and B. Benner) and the EPA (R. Merrill) and (2) the PhD thesis research of Ann Sheffield (U. of MD advisor: G. Gordon). In both of these studies, the isotopic and chemical composition of particulate polycyclic aromatic hydrocarbons (PAH) were investigated. Among the results were the facts that wood combustion contributes disproportionately to the PAH fraction of ambient particulate carbon, in comparison to motor vehicle emissions -- i.e., the "soot" carbon is not isotopically homogeneous with respect to chemical species. A principal result of the Sheffield thesis research was the first demonstrated correlation of ^{14}C with chemical (PAH) "markers" for auto emissions and woodburning. The exciting challenge ahead is to understand better the combustion chemistry behind these empirical (multiple linear regression) findings.

Isolation and ^{14}C dating of individual amino acids from ancient bones comprised the postdoctoral research of Tom Stafford. Painstaking isolation chemistry involving chromatographic separation of fulvic acids from the amino acids, followed by separation of the individual amino acids for radiocarbon dating, gave a reliable method for determining the age of ancient man and other ancient mammals exposed to varying degrees of diagenesis. Concordance between the individual amino acid dates and those of the purified collagen fractions appears to be the key criterion, long sought to ensure dating accuracy for skeletal remains.

Another powerful linkage between chemical and isotopic analysis for particulate studies has been found in the combination of AMS and laser microprobe mass spectrometry (LAMMS). Cooperating with the University of Arizona and the Microanalysis Group, we applied chemometric techniques to link the isotopic source signature of ambient particles with carbon cluster patterns obtained from individual combustion particles. In effect, ^{14}C measurements of bulk particles have been used to "calibrate" structural patterns for individual particles. A very important consequence of such intercalibration is the possibility of quantifying combustion sources for media (such as ice cores) in which particle concentrations are far below levels practicable for AMS measurements.

Fundamental studies in chemometrics in FY88 have addressed two issues of broad importance in analytical chemistry, namely, the treatment of multivariate chemical data having errors in two or more variables, and sampling strategies designed to optimize the information gained when one is constrained (e.g., by cost) by the number or types of measurements that may be performed. The first problem arises in many areas of chemical analysis, ranging from accurate evaluation of univariate and multivariate calibration functions to the estimation of parameters and uncertainties in multicomponent analysis. In cooperation with university and NIST statisticians and mathematicians, we are investigating the reliability of several alternative approaches to this problem. The study of optimal sampling design was engendered by a practical problem requiring selection of the "best" subset of IACP samples for mutagenicity testing and for ^{14}C measurement -- both relatively expensive techniques. By optimizing with respect to a reasonable "objective function", we were able to capture most of the potential information with less than half of the usual number of samples.

Significant contributions have been made during the year to quality assurance in analytical chemistry and to the basic concept of detection, including societal, historical, and technical aspects. This latter work is contained in chapters published in December 1987, in the ACS Symposium Series 361 volume on Detection in Analytical Chemistry (L.A. Currie, Ed.). Contributions related to quality assurance have come about through service on advisory panels for unversities, industries, other government agencies and national and international societies/commissions.

Future plans call for expansion of the atmospheric carbon program to regional and global studies, with initial emphasis on the CO-OH-CH_4 system. For this purpose, we have established contacts with scientists at the National Center for Atmospheric Research (NCAR) and the Dept. of Scientific and Industrial Research (New Zealand) to plan global sampling and organize complementary measurement programs. Research on standard reference photometry will be enlarged, as a result of improved detector capabilities, to investigate trace atmospheric levels of SO_2 and NO_2. LAMMS - pattern recognition research will be extended to additional types of carbonaceous particles, and we shall endeavor to utilize the information gained from our exploratory multivariate studies to learn more about the fundamental structural and mechanistic bases for the LAMMS spectra. We anticipate a conclusion to the chemometrics study on errors-in-variables, including recommended procedures for generating valid results and uncertainty estimates for such problems. Chemometrics research will be directed also during the coming year to investigating systematic approaches to the design and evaluation of the chemical measurement process, beginning with the selection of a problem having broad importance and significant multivariable and multicomponent aspects.

Lloyd A. Currie, Group Leader; Donna Barraclough, Arnold M. Bass, Ken R. Beebe, P. Ed Hare, George A. Klouda, James E. Norris, Will M. Ollison, Ann E. Sheffield, and Thomas W. Stafford.

2. Microanalysis Group: Overview

The Microanalysis Research Group carries out research to develop and apply microbeam analysis techniques for the chemical, morphological, and crystallographic characterization of matter on the micrometer and sub-micrometer spatial scales. The analytical techniques utilized are based on primary (excitation) beams of electrons, ions, or photons, and secondary (analytical) signals of x-rays, elastically and inelastically scattered electrons, elastically and inelastically scattered photons, or ions. The techniques used include electron probe microanalysis (EPMA), scanning electron microscopy (SEM), analytical electron microscopy (AEM) with energy dispersive x-ray spectrometry (EDS) and electron energy loss spectrometry (EELS), secondary ion mass spectrometry (SIMS), laser microprobe mass analysis (LAMMA), laser Raman microanalysis (LRM), x-ray diffraction (XRD) and polarized light microscopy (PLM).

Research is conducted on several aspects of each technique to (1) understand the basic physics of sample excitation by the primary radiation and of the propagation of the secondary radiation; (2) develop methods of quantitation; (3) produce reference materials and techniques as a means of disseminating developed technology; (4) apply results of the research to improve compositional mapping techniques; and (5) study specific analytical problems to support NIST and other government agency activities as well as national scientific priorities.

The 1988 fiscal year has been a particularly active year for the group, marked by significant expansion with concomitant new responsibilities in the areas of asbestos analysis and characterization of superconducting materials. Group members have been active in research in each of the major technical areas, including electron, ion, and photon beam techniques, with the following progress in each area.

I. Electron Techniques

(a) Electron Probe Microanalysis

The need for fundamental data to support advancement in quantitative analysis procedures is being met by the development of the electron/x-ray optical bench. The first version of this instrument, which incorporates a conventional scanning electron microscope column and both flow proportional and energy-dispersive x-ray spectrometers, has been successfully constructed and tested. The system has been evaluated with a preliminary series of experiments to measure the x-ray absorption function on pure element and binary compound targets.

Our activities in fundamental studies in electron microprobe quantitation are focussed on a detailed examination of theoretical aspects of models for matrix correction procedures for quantitative electron probe microanalysis. This work is complemented by efforts to re-evaluate and improve the standard computer algorithm for microprobe analysis.

This year marked the 20th anniversary of the publication of the international workshop on quantitative electron probe microanalysis held at NBS (NBS Special Publication 298, Quantitative Electron Probe Microanalysis), a meeting which is widely regarded as a watershed in the development of the technique. Because of the rapid progress in the past five years in new techniques of quantitative electron probe analysis we convened a new workshop in conjunction with the annual conference of the Microbeam Analysis Society (August 15-17, 1987). Experts from the U.S., Europe and Japan participated in detailed discussions on quantitative electron probe analysis, which will appear as a new NIST special publication on the topic.

The development of compositional mapping with the electron microprobe was continued with emphasis on combining wavelength-dispersive x-ray spectrometry (for sensitivity and spectral resolution of interferences) with energy dispersive x-ray spectrometry (for detection of multiple elements) to expand substantially our mapping capabilities. Compositional mapping was also applied to a variety of problems in materials science, with an especially large effort directed towards the study of bulk and thin-film high Tc superconductors. The compositional maps of these materials aided NIST (IMSE) scientists to understand limitations to the superconducting performance of these materials.

(b) Analytical Electron Microscopy

The first Standard Reference Material for AEM, a thin glass film (101 nm thick) containing major concentrations of Mg, Si, Ca, Fe, and O, designed for calibrating the x-ray spectrometer of the AEM for quantitative elemental analysis, was issued. Further research to produce additional films in this series, to expand the energy range of quantitative analysis, will be facilitated by the purchase of a large-beam ion sputtering apparatus. By having the sputtering apparatus in-house, better control of the experimental conditions to produce the potential SRMs will be possible. In addition, a new multichannel (parallel detection) electron energy loss spectrometer (EELS) has been added to the 200 keV AEM. This EELS instrument expands our capabilities for microanalysis of light elements, and provides the basis for developing and testing a new class of AEM standards specifically directed toward EELS microanalysis.

Two other related developments have substantially expanded our beam energy and beam resolution capabilities in analytical electron microscopy. First, a new 300 keV computer-controlled AEM has been procured to provide the in-house measurement basis for the airborne asbestos National Laboratory Accreditation Program (NLAP). Second, the National Institute of Standards and Technology/National Institutes of Health Nanometer Analysis Facility was dedicated in May. This facility is based upon a field emission scanning transmission electron microscopy (FE-STEM), which has the capability of forming a 1 nm analytical probe, in addition to imaging with probes as small as 0.5 nm.

(c) Asbestos Standards and Laboratory Accreditation Program

The Microanalysis Research Group has been active for ten years in developing and characterizing techniques for analyzing asbestos in air, water, and solid samples. In response to regulations by the Environmental Protection Agency, Occupational Safety and Health Administration, and laws propagated by Congress, we are standardizing the analytical methods used for checking abatement and compliance with state and Federal regulations for bulk and airborne asbestos. To accomplish this, we have set up a National Laboratory for Asbestos Analysis. Instrumentation for this laboratory includes x-ray powder diffraction, light microscopy, and transmission electron microscopy (TEM) systems with computer and image analysis support. We have hired four people with skills in polarized light microscopy, mineralogy, x-ray diffraction, crystallography, and transmission electron microscopy to perform characterization of standard methods and SRMs for asbestos analysis and to provide technical support for the National Laboratory Accreditation Program at NIST.

II. Mass Spectrometry Microanalysis

(a) Secondary Ion Mass Spectrometry

The Microanalysis Group has continued its vigorous research program in secondary ion mass spectrometry (SIMS). Our ion microscope has been upgraded by the addition of a resistive anode encoder image detector, a position-sensitive detector that can record single ion arrivals. A new control computer system based on an IBM-PC-AT was also installed. A major new program in SIMS will begin with the delivery of a time-of-flight secondary ion mass spectrometer that includes a pulsed liquid metal ion gun. This instrument will have an ultimate spatial resolution of about 200 nm, and the capability to detect ions of all masses for each pulse of the ion gun.

In the past year, SIMS has been used for a variety of applications, many of which are in the field of semiconductors. Progress has been made toward the first SRM for depth profiling by SIMS, a material which consists of ion-implanted boron in pre-amorphized silicon. This work is being done in collaboration with the Naval Research Laboratory (NRL) and the Aerospace Corporation. While characterizing a prototype material, several 'unknown' artifacts produced by the ion implantation process were detected. High-dose implantations of oxygen and nitrogen in silicon have been studied in collaboration with the Center for Electronics and Electrical Engineering (CEEE) and Sandia National Laboratory. Collaborative SIMS research has also been carried out on MeV Be implants in GaAs (with NRL) and on Fe implants in InGaAs (with George Mason University).

The imaging capability of the secondary ion microscope has been exploited in a study of the oxygen distribution in high Tc superconductors, which was shown to be highly non-uniform in samples in which the cations were also inhomogeneously distributed. A project is underway to measure local oxygen compositions more quantitatively using in-situ implantation of ^{18}O to provide a localized isotopic spike for a direct isotopic dilution measurement by SIMS.

A new thrust this year has been the investigation of secondary ion imaging of organic species in the ion microscope. A post-doc has been added to the group to advance this work. It is often assumed that intact molecular ions cannot be produced from a surface previously damaged by ion bombardment. We have found that a sufficient molecular signal is often available for useful imaging with the sensitive imaging detector that is now available on our machine, even after prolonged ion bombardment of an organic material. Studies in progress are designed to look at the effects of various parameters such as primary beam species and energy on the damage-induced decay of molecular ion signals from various model organic compounds.

(b) Laser Microprobe Mass Analyzer

We have continued to develop analytical methods and applications for the laser microprobe mass analyzer (LAMMA). Detailed studies have been carried out on the response of the conventional ion detector of the LAMMA, and a new detector has been designed and tested. A new computer-controlled sample stage has been designed which will permit more precise positioning of particle targets. Interelement effects on quantitative analysis have been studied, and the influence of sample geometry on ion signal has been evaluated. Recent research directions have been in utilizing pattern recognition techniques for analyzing and comparing the spectra of carbon aerosol particles that have been generated in the laboratory with particles that have been collected from the atmosphere for use in source apportionment studies. In another project, analysis of micrometeorite samples is underway using the laser microprobe, with the results to be correlated with those from analytical electron microscopy of particle thin sections.

III. Photon Beam Microanalysis

Research in Raman microprobe spectroscopy is centered on the application of micro-Raman instrumentation with monochannel (PMT/photon counting) and multichannel (optical array) detection in both fundamental and applied problems in molecular/structural microanalysis. The NIST-developed scanning Raman microprobe has been used this year in the study of several types of materials problems of high-technology interest (e.g., diamond films, superconductor ceramics, and carbon and polymer composites). The superior spectral resolution of this instrument has allowed the documentation of sharp structure resonances, both in the fluorescence and Raman emissions, of spherical microparticles, results which are of interest relative to the predictions of current theoretical models of inelastic scattering.

The multichannel Raman microprobe, based on spectrographic dispersion, has been upgraded this year with the acquisition of a state-of-the-art intensified diode array detection system. The improved performance capabilities of the instrument have been evaluated in measurements on microsamples (explosives, superconductors) potentially subject to time-dependent laser-induced modification, utilizing the multiplex advantage for short-time integration of weak Raman signals. This effort in getting the new system fully operational has been expedited with the help of Professor Thomas D. Schroeder of Shippensburg University in Pennsylvania who spent the summer with us.

IV. Image Processing

A major component of our research in quantitative microscopy involves the development of computer-aided imaging techniques. Important progress in this area includes the development of scatter plots for analysis of compositional maps with more than two compositional variables. This method permits rapid, quantitative evaluation of concentration relationships in images, and provides high sensitivity for the recognition of low-frequency events in such images. A critical advance supporting much of our image software activities has been the development of a fast machine-code version of the "BLOBBER" function, which is used to dissect images into basic units of contiguous picture elements sharing similar properties.

V. Particle Collection and Analysis

Experiments on characterizing particle aerosols have been undertaken in conjunction with external collaborators, including Professor Gentry of the Department of Chemical Engineering of the University of Maryland, to study collection of asbestos on filter media. Work is proceeding to characterize fully the sub-micrometer particle collector developed several years ago. We have also developed important particle handling methods, with detection of selected elements by nuclear track techniques.

Future Plans:

An amazing range of new research opportunities has opened up to group members as a result of the newly available instrumentation. The 300 keV analytical electron microscope, NIST/NIH scanning transmission electron microscope, and time-of-flight secondary ion mass spectrometer will provide opportunities to perform analyses which can be spatially-resolved at the nanometer scale. Many new problems in quantitation and standardization will have to be addressed to advance into this area. We will explore the fabrication of the new class of thin-film Standard Reference Materials for these analytical applications by means of the new ion beam sputtering apparatus. We will continue as well to improve the established analysis techniques such as electron probe microanalysis, secondary ion mass spectrometry, laser microprobe mass spectrometry, and laser Raman microanalysis.

Dale E. Newbury, Group Leader; Adville A. Bell, David S. Bright, Peter H. Chi, Edgar S. Etz, Robert A. Fletcher, J.G. Gillen, K.F.J. Heinrich, S.M. Hoeft, M.D. Johansen, Ryna A. Marinenko, Robert L. Myklebust, F. Scott Pereles, J.M. Phelps, Cindy J. Poston Patrick J. Sheridan, David S. Simons, John A. Small, Eric B. Steel, Barbara Thorne, Shirley Turner, and Jennifer Verkouteren.

3. X-Ray Fluorescence Group: Overview

The principle objective of the X-ray Fluorescence Group is to maximize the accuracy and sensitivity of the analysis of elemental composition in a variety of materials. A major, ongoing effort is devoted to improving first principle methods of corrections for interelement matrix effects for non-destructive assay. To this end, we are constantly updating the computer program NBSGSC developed by us to take advantage of more accurate fundamental parameters when they become available. We plan to publish a major update of NBSGSC in late 1989.

We have investigated several approaches to increase analytical sensitivity. First, we have characterized several batches of commercial filters to which we have covalently bonded specific chelating groups, such as dithiocarbamate and oxine, for the purpose of preconcentrating trace elements prior to analysis. So far, this approach has met with limited success because of the variability of the elemental capacity of these derivatized commercial filters. We are now seeking ways to increase the capacity and improve the reproducibility by making the derivatized filters directly from paper pulp, working closely with D.B. Blanchard and K.F. Hermsen of the NIST Fibrous Systems Division. In related work, we are continuing our efforts with H.M. Kingston of the Inorganic Analytical Research Division to develop rapid HPLC separation methods for sample preparation prior to preconcentration.

A second approach to increase analytical sensitivity has been initiated this year by construction of a total reflection x-ray spectrometer. In early 1988, we published a paper describing the sensitivity (sub-ppb detection limits) of this new instrumental technique for XRF analysis using a very bright synchrotron source. The principle components for a laboratory system consist of a high-intensity rotating anode x-ray source, a double-crystal spectrometer, and a solid-state detector. We have purchased a double-crystal spectrometer and interfaced it to the rotating anode x-ray source and are focusing efforts to demonstrate the sensitivity of this system.

Several sets of thin films have been completed for use in interlaboratory quality assurance programs which employ x-ray fluorescence methods of analysis. The purchase of a focused ion-beam sputtering system this year will make the fabrication of such films much easier in the future. We intend to complete the development of zinc sulfide thin films for XRF calibration during 1988, so that we can begin production of these films as SRMs next year.

A major part of our work continues to be the homogeneity testing and quantitative analysis of a wide variety of materials of special interest to the Office of Standard Reference Materials. Among the new materials we completed this past year was NBS/SRM 2704 (Buffalo River Sediment) where we contributed to the NBS certification of twelve elements. Other materials analyzed consisted of minerals (SRM 600-Bauxite), alloys (SRM 1219, 1250, 868, 1276a), cements (SRM 1884-1889), flows older powder (SRM 1129), and oils (SRM 1624b).

Future Plans:

An NIST Research Associate from Kevex Corporation will join the XRF group in November 1988, to work on the development of instrumentation and software for performing x-ray imaging compositional mapping. This will be a new long-term area of research for us. The use of a micro-focus x-ray tube or a crystal-focused high-intensity source such as the rotating anode to obtain x-ray beam diameters of 10 μm or less makes this a viable technique for obtaining useful chemical compositional maps.

Activities of the Past Year:

(1) Determined performance of filters impregnated with dithiocarbamate and oxine ligands for trace element preconcentration.

(2) Completed two sets of thin films for XRF laboratory quality assurance evaluation.

(3) Completed XRF analysis of NBS/SRM 2704 (Buffalo River Sediment) for NBS certification.

(4) Interfaced a new double-crystal spectrometer to a rotating anode source for performing total reflection XRF analysis.

Peter A. Pella, Group Leader; Anthony F. Marlow, John Sieber, and Gerald A. Sleater.

4. Gas Metrology Research Group: Overview

The Gas Metrology Group and the Analytical Laser Spectrometry Group have been combined to form the Gas Metrology Research Group. The combination is operating smoothly since both groups are involved in the same basic area, preparation and analysis of gas mixtures, and the goals of the combined group include the same objectives as the two individual groups.

The Gas Metrology Group conducts research on accurate preparation methods and highly precise and definitive analytical techniques for the development of primary gaseous standards. The research and standards are applied to the quantitative evaluation of gas mixtures ranging in concentration from the percent level to the one part-per-trillion (ppt) level and in complexity from single to multicomponent gas mixtures.

Although the metrological outputs of the Group are primarily focused on the certification of a wide variety of inorganic and organic gas Reference Materials (RMs) and Standard Reference Materials (SRMs), a substantive portion of our activities involves measurement research covering the broad range of gas analysis. Specific attention is given to detailed evaluations of preparative and measurement uncertainty, assessments of the long-term stability of gas mixtures, and the development of fundamental data on the spectral, chromatographic, and detection properties of gas mixtures.

Preparative techniques used to develop primary gravimetric standards for assuring the accuracy of trace gas measurements are based on absolute gravimetry involving pressure-vacuum manifold systems, gas blending, and other methodologies. Verification techniques to assess the efficacy of primary standards or a suite of primary standards include the use of dynamic dilution, permeation device systems, statistical evaluation of correlation curves, and measurement methods such as spectroscopic absorption coefficients. Analytical techniques include: gas chromatography (GC); mass spectrometry (MS); GC/MS; non-dispersive infrared analysis; chemiluminescence spectrometry; tunable diode laser absorption spectroscopy (TDLAS) and a variety of ancillary analytical systems for the determination of trace gaseous impurities. Data acquisition and statistical data evaluation command a substantial portion of the Group's attention.

The gaseous standards developed by the Group are used to certify RMs or SRMs that serve as primary calibrants for national and state regulatory programs, industrial, institutional, Federal measurements, international collaborative programs, and global monitoring programs. The Group, working through the Gas and Particulate Science Division, is responsive to and interacts with gas measurement and standards needs of other agencies, industrial organizations, and standards-setting bodies at the local, state, and national levels. Group members routinely provide advice and guidance to the private sector, and interact with investigators on gas measurements and standards on a world-wide basis. Based on its expertise in gas measurements and standards, the Group also performs a limited number of gas analyses for external organizations.

During FY88, the Group's SRM work resulted in the certification of twelve 50-cylinder batches of gaseous SRMs, including one new SRM and a new RM for multicomponent volatile toxic organic compounds, ranging in concentration from 10 ppm to 5 ppb. Approximately 300 permeation tubes for SO_2 and NO_2 were also certified. During this period, the Group's research activities included: (1) the final development and evaluation of the procedure to prepare primary gravimetric standards to certify CO_2 in air mixtures used in global monitoring programs for atmospheric CO_2; (2) the development of NIST-traceable standards containing up to 6 volatile toxic organic compounds in the ppt to ppb range to provide data quality assurance for the state of CA; (3) a calibration procedure for the TDLS to analyze for low concentration levels of H_2O_2; (4) development and testing of a system to generate the atmospherically important trace constituent HONO, and (5) a study of the reaction/equilibrium of $NO_2/H_2O/HNO_3$ in high pressure compressed gas cylinders.

The important program to provide carbon dioxide in air SRMs for use by the scientific community and especially the World Meteorological Organization (WMO) in monitoring the increase in global CO_2 concentration is continuing. During the year, three aspects of the program have been finalized: (1) a primary standards set of cylinder mixtures of CO_2 in air prepared by gravimetry; (2) the recertification of five batches of CO_2 in air SRMs; and (3) the determination of the concentration of carbon dioxide in mixtures of CO_2 in air by isotope dilution mass spectrometry (IDMS). During FY87, research was performed in developing single and double dilution procedures for the gravimetric preparation of CO_2 in air mixtures in high pressure gas cylinders. This resulted in two suites of standards which proved to be slightly but statistically different. Combining the two suites would have resulted in a higher analytical uncertainty than appropriate. Continued research showed that in one step of the double dilution procedure, the CO_2 was not quantitatively swept into the containment cylinder. When this was rectified the standards produced by the single dilution method were indistinguishable from those produced by the double dilution procedure. These new primary standards were then used to recertify the CO_2 in air SRMs. The work in the IDMS determination of CO_2 was concluded this year. All aspects of the gas handling and measurement systems were evaluated, some were changed or modified, and all required calibrations were performed. The results from the analysis by IDMS agree within the measuremenet uncertainty with the results generated by use of the gravimetrically prepared standards. This is important because it demonstrates that there is no bias in the primary gravimetric standards.

Another important program, the development of reference materials for volatile toxic organic compounds, is continuing and has been expanded this year to include mixtures at much lower concentration levels than in the past. Primary standards containing up to eighteen organic compounds, each at the 15 parts-per-trillion (ppt) level, have been developed as SRMs and for the California Air Resources Board. Working with mixtures at the low ppt level required development of gas chromatographic procedures that incorporate an electron capture detector, which is extremely sensitive for certain classes of compounds. Research has also been completed in the development of a 24-component standard containing compounds from the EPA's Superfund Hazardous Substance list.

Hydrogen peroxide is an important trace atmospheric constituent of interest to EPA. It is difficult to generate calibration standards containing known amounts of H_2O_2; thus a procedure was developed to generate a mixture of known amounts of H_2O plus H_2O_2 in air and then pass it through a spectroscopic cell. The amount of H_2O is determined by observing a known absorption band of H_2O with a well-known absorption coefficient and the amount of H_2O_2 calculated by difference. The spectrometer, in this case a TDLS, is then calibrated by observing a band of H_2O_2 and determining its absorption coefficient.

Another trace atmospheric constituent which plays a significant role in atmospheric chemistry is HNO_2 (HONO). No reliable calibration standards exist for this gas; therefore, a system was developed similar to the one used to generate HNO_3 (i.e., dilute gas mixture of $HCl + AgNO_3 \rightarrow AgCl + HNO_3$). The silver nitrate ($AgNO_3$) was replaced by silver nitrite ($AgNO_2$) and a dilute gas mixture of HCl passed over it. The output of this generator was analyzed for HONO content using TDLS; only about 3% of what was expected was found. Additional work is needed to establish conditions that affect HONO generation.

Cylinder mixtures of standards are frequently easier to use than more complex generation systems; therefore, we investigated the possibility of providing cylinder mixtures of HNO_3 even though we developed the HNO_3 generation system. Mixtures of NO_2 in air were doped with H_2O to cause the reaction $H_2O + NO_2 \rightarrow HNO_3$. An equilibrium mixture of $NO_2/HNO_3/H_2O$ exists in these cylinders which are being studied for the stability of the NO_2 and the HNO_3 content.

Other accomplishments of this year included: the use of the HNO_3 generator with a dilution system to provide calibration mixtures of 1 ppb HNO_3 in air; the determination of the lower detectable level of the TDLAS for many compounds (CO, SO_2, OCS, CS_2, NO_2, HNO_3, CO, CO_2); the continued upgrade of one of two TDLAS systems so that it can be more easily used for analytical work; the re-evaluation of twenty-five primary standards to provide the Western Primary Standards Laboratory of the U.S. Navy with standards to support their effort in ambient monitoring of enclosed areas of Navy installations and vessels; and, the development and evaluation of thirty new primary standards to analyze breathing oxygen standards for Naval aviators.

A joint program between NIST and the Motor Vehicle Manufacturers Association (MVMA) has been established to produce seven new SRMs and to restock four existing SRMs all of which are needed for either engineering work in the auto industry or to provide standards for EPA emission compliance measurements. The MVMA has supplied a research associate to work at NIST on this program.

Future Plans:

Our future plans are to: develop dynamically prepared calibration standards of five sulfur gases (SO_2, H_2S, COS; CS_2, and $(CH_3)_2S$) and the analytical methodology to measure these gases at the 0.5 to 1 ppb level; continue work on doped "zero gas"; establish better measurement capability for water vapor in gases; develop a more sensitive statistical model to evaluate outlying or drifting standards in a suite of standards; determine feasibility of producing stable, dry HNO_3 cylinder mixtures using the output of the HNO_3 generator; continue to improve quantitative capabilities of TDLS; and establish a more rigorous quality assurance program to assess long-term stability of the more than 100 primary standards of the Toxic Organic Gases program.

William D. Dorko, Group Leader; Barry C. Cadoff, Patricia A. Johnson, Steve Krauss, Rudolph von Kelly, Gerald D. Mitchell, W. Robert Miller, Richard D. Myers, Linda Nunnermacker, George C. Rhoderick, Robert L. Sams, James E. Suddueth, Nicholas Sylvain, R. Michael Verkouteren, and Walter L. Zielinski, Jr.

B. Selected Technical Reports
(Gas and Particulate Science Division)

1. The Use of Experimental Design Methodology for Effective Sample Selection: Application to Aerosol Source Apportionment

K.R. Beebe and L.A. Currie

As part of the Integrated Air Cancer Project (IACP), the EPA used approximately 80 aerosol samples from Boise, Idaho to estimate the effect of wood burning and automobile emissions on the mutagenic activity in the atmosphere. Forty samples were collected from each of two sites, Elm Grove Park (a residential site) and Fire Station (a roadway site), over two, 12-hour sampling periods. For each sample, the concentrations of potassium (K) and lead (Pb) were measured by x-ray fluorescence spectroscopy. These constituents were used as unique tracers for wood burning and automobile emissions, respectively. The mutagenicity of the organic fraction of the aerosol samples was measured by EPA, and multiple linear regression was used to estimate the effect of the tracer elements on the mutagenicity.

Our involvement in the study was in testing the validity of the results based on the elemental (K,Pb) tracer model using an independent measurement for source apportionment (^{14}C). Theoretically, validation would be best achieved by using all 80 samples. However, it was deemed impractical to analyze all the samples for ^{14}C. Therefore, it was necessary to choose a smaller subset of samples for analysis. This subset selection was subject to two constraints: a) equal representation from the four site-periods, and b) an overall "cost" (time, personnel, analytical expenses, etc.) constraint in measuring the ^{14}C. The second constraint set a pro-tem maximum of 9 samples from each site-period to be used for validation. The major concern became the selection of an appropriate subset of samples that would effectively use the available resources while maximizing precision in the final model.

The two basic points that needed to be addressed were: a) What are the best samples to use? and b) How much is the precision in the model compromised by using a reduced set of samples?

For a given number of samples selected for ^{14}C measurement, we were concerned with selecting the "best" subset. "Best" is generally defined in terms of an "objective function" or measure which exhibits a maximum or minimum for the chosen samples. The nature and magnitude of this function can then be related to the adequacy of the validation test. We faced two questions: which objective function to employ, and how to select the best subset of samples. To answer these questions, we first chose a validation model as follows:

$$C_i = b_0 + b_1K_i + b_2Pb_i + e_i$$

where C_i is the combined carbon (fossil and wood source); K_i is the potassium concentration; and Pb_i is the lead concentration, all for the i_{th} sample. For linear models such as the one considered here, a natural choice of objective function is the determinant of the Fisher information matrix $|X'X|$. This approach, using what is termed a "D-optimal" criterion, yields the minimum volume confidence ellipsoid for the parameter estimators. In other words, the final subset of samples will yield a model with good properties, i.e., relatively small standard errors (SE) for all of the model parameters (b_0, b_1, b_2).

The following algorithm, based on a step-wise selection procedure using the D-optimal criterion, was used to select the subsets:

We began by choosing two samples (by a replacement design) from the 20 samples at each site and period. To this set we added a third sample from among the 18 remaining samples, and then calculated the resulting determinant. This initial model was designated an N = 3 model as three samples were used to calculate the determinant. This was repeated 18 times, each time using a different sample from the pool of 18. The sample that yielded the best determinant (maximum) was retained and the resulting three samples were used as the best N = 3 subset. Next, one sample at a time was added to the N = 3 subset from the remaining 20-3 = 17 samples until an optimal N = 4 subset was obtained. This process was repeated until the optimal set of nine samples was selected.

To evaluate the reduction in precision resulting from the use of a smaller set of samples, we examined the resulting SEs for the model coefficients as the samples were added one at a time. The value of the SEs decreased monotonically and reached a plateau at approximately N = 8 for all of the model coefficients. It was clear that little is gained by going beyond the optimal set of 9 samples. For example, the N = 13 model for one typical site-period sample set yielded further SE reductions of only 4% for b_0, 2.7% for b_1, and $< 0.1\%$ for b_{b_2}.

Selection of samples for measurement according to sound experimental design principles can greatly increase the information gained per unit cost. When rather expensive or time-consuming operations are involved, such planning is vital to (a) identify the most cost-effective measurement (sampling) scheme, and (b) assess in advance the adequacy of the plan.

2. A New Approach to the Determination of the Origins of Individual Carbonaceous Particles through Accelerator Mass Spectrometry (AMS) and Laser Microprobe Mass Spectrometry (LAMMS)

L.A. Currie, R.A. Fletcher, and G.A. Klouda

Parallel and "hybrid" analytical measurements applied to common samples can often provide far more information than a simple "sum of the parts." Such is the case for AMS-LAMMS, as applied to atmospheric combustion particles ("soot"). AMS measurements of ^{14}C have served a critical function in our research on the origins of atmospheric gases and particles, in that it is a direct and unique tracer for biospheric ["living"] carbon. When combined with carbon mass determinations of selected compounds, such measurements yield direct estimates of fossil and biogenic source contributions. The great strength of LAMMS is that it allows one to discern structural information of individual carbonaceous particles, covering a broad range of molecular weights. Interpretation of the rather complex LAMMS spectra, however, is not facile.

We have been able to take advantage of the strengths of each analytical technique through their linkage. Beginning with laboratory experiments ("test burns") of single source combustible materials, we have begun to establish "fingerprint" characteristics of the resultant, high molecular weight soot particles. To obtain this material, we took advantage of test burns by the NIST Center for Fire Research [G. Mulholland], in support of the Nuclear Winter program. Particles from the combustion of heptane, cured wood, and polyurethane were collected. LAMMS positive and negative ion mass spectra were examined for pure graphite, and combustion particles from each of these source types. Pattern recognition techniques (selection of discriminating masses followed by 2- and 3-dimensional principal component mapping) were successfully applied to the positive ion spectra for combustion source identification. When these patterns were compared to ambient atmospheric particles which were selected to be primarily fossil fuel or biogenic (wood fuel) in origin, on the basis of ^{14}C bulk analysis, discrimination failed. Evidently, assumptions concerning the composition of laboratory combustion particles, in contrast to those in the atmosphere (from real motor vehicles and woodstoves), are not fully valid.

Turning to the negative ion spectra, especially to cluster-ion features such as C_n^- and C_nH^-, we found consistent patterns for field and laboratory particles showing successful discrimination of the soot from wood and fossil fuel sources. It should be noted that such discrimination is not necessarily a trivial matter, for the high molecular weight soots tend to be largely graphitic in structure, regardless of fuel type, as a result of the acetylenic radical polymerization processes that occur in the flame. Validation or calibration of the source identification patterns for ambient particles therefore requires a quantitative discriminator of known reliability such as ^{14}C.

After investigating the validity of "end member" identification in the field, we took advantage of ^{14}C measurements on a suite of samples collected in Albuquerque as part of the EPA's Integrated Air Cancer Project to assess the relative contributions from motor vehicles and woodburning to the serious levels of carbonaceous pollutants and mutagens in the wintertime urban atmosphere. Negative ion LAMMS spectra were obtained from individual particles from bulk samples that had been collected for ^{14}C measurement. A very important outcome of this dual method study was a LAMMS pattern calibration curve, where quantitative changes in selected pattern indices (cluster ion ratios) were related by regression to the ^{14}C concentration, which in turn gave a direct measure of the wood/fossil fuel source apportionment. This approach thus transfers the isotopic tracer information from the 10's of μg-C level to the pg-C level, as the points on the calibration curve were obtained with 3 - 5 fine particles each.

The next goals of this project will be to confirm the findings in other airsheds and possibly in remote atmospheres, and to begin to understand the physicochemical bases for the combustion source related cluster ion patterns. Besides the prospect of learning more about these combustion and laser plasma processes, we anticipate important applications to carbonaceous particle origins in areas, such as the stratosphere and cryosphere, where concentrations are too low for direct AMS measurements.

3. Improved Accuracy in the Radiocarbon Dating of Bone and the Tracing of Atmospheric Carbon via Micro-organic Isotopic Measurements

G.A. Klouda, T.W. Stafford, L.A. Currie, A.E. Sheffield, and D. Barraclough

Our accomplishments this past year include the development and application of micro-chemical separation techniques for solving environmental radiocarbon problems. In atmospheric chemistry, the application of the ^{14}C tracer technique to individual compounds and chemical classes at the microgram level has demonstrated that specific source information of improved accuracy is gained through chemical speciation. Similarly, accurate ages of poorly preserved fossil bone have been obtained by dating specific amino acids extracted from bone collagen. These studies involving ^{14}C measurements at the microgram level are possible only through the use of accelerator mass spectrometry (AMS).

Investigations into the origin of environmentally important atmospheric pollutants, e.g., extractable organic material (EOM), polycyclic aromatic hydrocarbons (PAH's), elemental carbon (C_e), CO, and excess CH_4, have involved micro-chemical separation techniques. AMS ^{14}C results of EOM and PAH fractions extracted from wintertime Albuquerque, NM, source samples representing 1) motor vehicle emissions, 2) wood-burning emissions, and 3) a mix of these two sources compared well with estimated impacts. A more extensive study of Albuquerque PAH's was completed this year (A.E. Sheffield) using ^{14}C measurements of this fraction to validate the use of single PAH's as tracers of wood burning and motor vehicle emissions. The ^{14}C tracer technique for source apportionment is currently being applied to total carbon, EOM, and C_e collected in Boise, Idaho, for the EPA Integrated Air Cancer Project (IACP).

Emphasis was also placed this year on the chemical characterization of the so-called elemental carbon fraction of air particles where this fraction has previously been operationally defined. Our approach utilizes 70% HNO_3 to remove the organic carbon from the particulate material followed by thermal combustion of the residue to CO_2 for quantitation by manometry in a calibrated volume. The reproducibility of this technique is 5-10% and results agree to within ~7% of the thermal optical technique. An important question remaining, and currently under investigation, is the quantitation of polymeric and graphitic carbon; both are assumed to make up the non-extractable and non-wet-oxidizable carbon fraction.

The selective oxidation technique to separate CO and CH_4 from 0.1 m^3 air, previously developed for urban atmospheres, has been successfully applied to remote "clean air" samples. This pilot study involved samples collected over the Amazon Basin (by aircraft) and at a high elevation site (ground based) in Colorado to evaluate the technique for pristine air samples where the concentration of CH_4 was ~1.7 ppm and that of CO was ~150 ppb. Additionally, the atmospheric CO_2 cryogenically scrubbed from the gas stream was isolated for ^{14}C measurement. Methane results for these clean air samples substantiated estimates that background CH_4 is largely biogenic in origin. These results are also in accordance with results of Wahlen et al. 1987. Plans are to test this separation procedure at higher flow rates to allow for processing 1 m^3 air samples. The increase in sample size will enable ^{14}C measurements on background CO at concentrations ca. 50 ppb and improve the precision of $^{14}CH_4$ measurements.

In comparison, CH_4 results from a number of eastern U.S. cities and two western cities suggest that the excess urban CH_4 is largely of fossil origin. Additionally, measurements of ^{13}C in CH_4, and other trace measurements of gases, e.g., N_2O (in collaboration with Gas Metrology Group), are under investigation for their value in the identification of source strengths. We plan next to apply this micro-chemical technique to the investigation of the global CH_4 and CO cycles.

In the fields of archaeology, anthropology, and geochemistry, radiocarbon dating of selected chemical fractions has shown great promise in situations where the presence of exogenous material may lead to inaccurate dates. During this past year, postdoctoral work by T.W. Stafford included the development of a fractionation scheme to isolate specific amino acids from fossil bone for accurate radiocarbon age determinations when the quality of preservation is in question.

Amino acid micro-chemical dating of fossil bone has been applied to known-age (11,000 yr) mammoths. Our hope was to understand the diagenetic differences between collagenous and non-collagenous fossil bone. Through micro-chemical separations, single amino acids were isolated using HCl elution from cation exchange resin. These fractions were then combusted to CO_2, and converted to graphite or FeC targets for ^{14}C AMS dating. Results suggest that dating of fossil bone that has been poorly preserved (containing little collagen) could substantially underestimate the age. In contrast, valid dating was demonstrated when residual collagen and isolated amino acids gave concordant ages.

Critical to these dating and tracer studies which involve multiple chemical steps is quality control and estimations of overall uncertainties. A PC-database has been established for this purpose. The database allows one to learn more about the chemical measurement process and the means to minimize the estimated overall uncertainty.

4. Application of Radiocarbon Measurements and Multivariate Analysis to the Source Apportionment of Polycyclic Aromatic Hydrocarbons

Ann E. Sheffield, Lloyd A. Currie, George A. Klouda, and Glen E. Gordon (University of Maryland)

The radiocarbon tracer technique was applied to the study of atmospheric, particle-borne polycyclic aromatic hydrocarbons (PAHs) in Albuquerque, NM. Fifty-eight samples were collected during December, 1985. One sampling site was located in a residential neighborhood, and a second site was near a busy roadway intersection. Fine particles were collected from about 6:00 - 18:00 (day) and 18:00 - 6:00 (night). Residential wood combustion (RWC) for home heat is common in Albuquerque, and we expected that the impact of RWC would be highest at night, when temperatures are lower and people are more likely to be home. Motor-vehicle emissions were expected to peak during the day, when traffic is heavier. Motor vehicles, a fossil source, and RWC, a modern source, are the only significant sources of PAHs in Albuquerque.

The PAH-fraction was isolated from each sample by solvent extraction followed by liquid chromatography. Levels of individual PAHs were determined by gas chromatography (GC) with flame ionization detection, and compound identifications were confirmed by GC/mass spectrometry. Sixteen samples were selected for radiocarbon analysis on the basis of a preliminary Factor Analysis (FA) and other relevant data. The PAH-fractions from the chosen samples were analyzed for ^{14}C by Accelerator Mass Spectrometry (AMS) using facilities at the University of Arizona.

Several compounds associated with softwood combustion were identified in the samples. The most abundant of these were the methyl ester of abietic acid (MABA), the methyl ester of dehydroabietic acid (MDHA), and 1-methyl-7-isopropylphenanthrene ("retene"). Abietic acid and its methyl ester are components of pine resin which decompose during combustion and in the atmosphere to give retene. Retene has been suggested as a tracer for softwood combustion, as has MDHA, an intermediate compound in the reaction. A number of common, unsubstituted PAHs were also identified, including benzo(ghi)perylene (BGP), a potential tracer of motor-vehicle emissions.

The radiocarbon data were used to calculate the fraction arising from RWC (f_{RWC}) in the PAH-fractions for the sixteen samples analyzed by AMS. For each sample, normalized BGP concentrations were calculated by dividing the observed BGP concentration by the sum of the concentrations of all PAHs in that sample. These normalized BGP values gave strong, negative correlations with the f_{RWC} data, which supports the use of BGP as a motor-vehicles tracer in Albuquerque. While no single compound associated with softwood combustion correlated with f_{RWC}, when the concentrations of MABA, MDHA, and retene were added to give a single value ("ADCS"), the normalized ADCS values gave strong, positive correlations with the radiocarbon data. Presumably, the relative levels of MABA, MDHA, and retene are determined by a number of factors (combustion temperatures, atmospheric chemistry, etc.), but their sum, ADCS, is less sensitive to such variables and can serve as a tracer for RWC.

A Factor Analysis, performed on PAH data for 55 samples, indicated that two factors explained 95% of the variance in the data set. One factor, attributed to RWC, had high loadings of ADCS and other softwood products as well as low-molecular-weight PAHs such as fluoranthene and pyrene. The second factor, attributed to motor-vehicle emissions, had high loadings of high-molecular-weight PAHs, including BGP. Medium-weight PAHs such as benzo(a)anthracene and chrysene had moderate loadings on both factors, which suggests that both emission sources contribute significantly to these species.

A combination of Multiple Linear Regression (MLR) and Target Factor Analysis (TFA) were used to estimate source profiles for RWC and motor-vehicle emissions. These profiles were used to perform Chemical Mass Balances (CMBs), a procedure which estimates how much of each compound in a sample is due to each source. For samples with a high RWC contribution (i.e., large f_{RWC}), RWC dominated the lower- and medium-molecular-weight PAHs and contributed somewhat to the heavier PAHs. However, when the source mixture was more balanced (f_{RWC} = 55%), motor-vehicle emissions dominated the heavy and medium-weight PAHs, and both sources contributed roughly equal amounts of the light PAHs. For the samples analyzed by AMS, the RWC contribution predicted by CMBs give a strong, positive correlation with the f_{RWC} values.

In summary, both statistical methods (FA, MLR, TFA, and CMBs) and direct measurement (^{14}C analysis) were used to investigate the sources of PAHs in Albuquerque. While statistically based source apportionment of PAHs is not new, the results have been subject to question because the degree to which PAHs degrade or are formed in the atmosphere is poorly understood. Here, the radiocarbon results provide a critical, independent measure of the source contributions and lend credibility to the statistical modeling results.

5. Maintaining the Primary Ozone Standard for the Domestic and International Communities

A.M. Bass and J. Norris

Since 1976, NBS has maintained an ozone standard calibration facility based on ultraviolet absorption photometry. In 1982, the original photometer was replaced by an instrument of new design and greatly improved performance. The new Standard Reference Photometer, which was developed as a collaborative effort with personnel from the Environmental Protection Agency (EPA), is capable of performing assays of ozone samples with an accuracy of ±1.5%, which is the accuracy to which the ozone ultraviolet (253.7 nm) absorption coefficient is known. The imprecision of such measurements is <1.0 ppb over the concentration range of 0 to 100 ppb, and $<1\%$ over the range 100 to 1000 ppb. The stability of the instrument is indicated by a standard deviation of 0.4 ppb for 20 repetitive measurements of a fixed ozone concentration over the working concentration range of 0 to 1000 ppb of ozone.

The stability and accuracy of the instrument led the EPA to adopt the NBS ultraviolet ozone photometer as the instrument for primary ozone calibrations in the EPA regional laboratories. The EPA requested NBS to construct ten of the NBS Standard Reference Photometers in order to establish their integrated, internally consistent calibration network for environmental monitoring. The first instrument was certified and delivered in 1982; eight more instruments have been delivered and installed since then, and the final one will be in place by the end of 1988. A regular schedule of intercomparisons between the EPA laboratory standard instrument and the NBS Standard Reference Photometer assures the traceability of measurements in the EPA network to the NBS primary standard.

During the past year we have similarly provided standard reference photometers to the National Swedish Environment Protection Board and to the Canadian Atmospheric Environment Service. These will serve as primary standards for Scandinavia and Northern Europe, and for the Canadian government network. Periodic comparisons with the NBS primary standard will assure the integrity of the ozone standard in the international community.

6. Ion Implantation Artifacts Detected by Secondary Ion Mass Spectrometry

D.S. Simons, P. Chi, J.F. Knudsen (The Aerospace Corp.), and H.B. Dietrich (Naval Research Laboratory)

Secondary ion mass spectrometry (SIMS) is commonly used to measure the depth distributions of dopants in semiconductors, where the dopant is introduced by high energy ion implantation. Often SIMS is used to study the redistribution of the dopant brought about by subsequent thermal processing. In other cases, the extent of ion channeling in a crystalline substrate is of interest, when the incident ion has been intentionally aligned along a high symmetry axis. For these types of studies it is usually assumed that the ion implanter is delivering a pure beam of the specified ion at a well-defined energy and current. Research done in our laboratory during the past year shows that this assumption is not always valid, and that SIMS can be a very useful diagnostic tool for detecting unexpected artifacts of ion implantation.

A series of arsenic implants in silicon, with implantation energies ranging from 25 keV to 200 keV, were profiled by SIMS. The depths of the peaks in the arsenic implant profiles were plotted against the stated implantation energies. A plateau in the data was seen between 50 and 100 keV. This anomalous behavior motivated a direct measurement of the accelerating voltage by use of a high voltage resistive divider chain. It was discovered that the energy meter on the implanter was not giving a reading proportional to the accelerating voltage, and that the energy was overstated for values in excess of 50 keV, just as the SIMS measurements had suggested.

Another example is related to a project designed to produce a Standard Reference Material for depth profiling measurements by SIMS. The material selected for evaluation is amorphous silicon that has been ion-implanted with ^{10}B at an energy of 50 keV and a dose of 1×10^{15} atoms/cm^2. The ^{10}B isotope was chosen because independent profiles can be measured by thermal neutron depth profiling (NDP). Amorphization of the silicon was carried out by implanting ^{28}Si at several energies up to 400 keV and at doses in excess of 10^{15} atoms/cm^2.

In one test sample it was found that the dose of ^{10}B was only 80% of the desired value, the remaining 20% being ^{11}B. The ratio of doses of the two isotopes was determined from the SIMS profiles of the two isotopes, whereas the absolute value of the ^{10}B dose was measured by NDP. In this case, the ion source of the implanter produced a relatively weak boron beam so a large mass-resolving aperture had been used to reduce the implantation time. However, this had the additional effect of allowing an unacceptable amount of ^{11}B to be implanted along with the ^{10}B.

In this same experiment it was noted that the background level of ^{10}B in the SIMS profile was higher than expected. A molecular ion interference at m/z 10 was suspected, possibly ^{9}BeH^{+}. A SIMS profile of ^{9}Be was taken along with ^{10}B. A surprisingly large beryllium signal with an unusual 3-peak structure was seen, which gave a clue to the origin of this contamination. Since the amorphization of the silicon wafer had been done by implanting ^{28}Si at three different energies, it was very likely that the beryllium had been unexpectedly introduced during the Si implantation. The cold cathode ion source of this implanter contains beryllium components that are sputtered by the discharge, and silicon had been introduced into the source as SiF_4 gas. Thus, beryllium was being implanted as the molecular ion ^{9}Be^{19}F^{+} along with the ^{28}Si. Since the level of BeH^{+} detected in the SIMS spectrum is typically between 0.1% and 1% of the Be^{+} signal, the beryllium present in this sample explains the high background level at m/z 10.

7. Electron Optical Bench for the Measurement of Fundamental X-ray Parameters

J.A. Small, D.E. Newbury, R.L. Myklebust, and K.F.J. Heinrich

Since the development of the electron microprobe by Castaing in 1951, quantitative x-ray microanalysis has evolved into one of the most powerful methods of spatially resolved analysis. For most routine analyses, the x-ray generation, absorption, and detection processes are well understood and correction procedures can be used to perform routine quantitative analyses at a relative accuracy of ±2%. There remain, however, several areas of microanalysis for which the electron beam-specimen interaction and the x-ray generation and absorption are not well known. These areas include the analysis of particles and thin films, the analysis of specimens containing light elements such as oxygen, and the analysis of specimens by the use of low energy electron beams. One of the main limitations to further improvements in these areas is that our knowledge of the various physical interactions is derived principally from experiments and theoretical studies performed in the period 1920-1960. The topic of medium energy (2-50 keV) electron-target interactions has not been rigorously studied since that time. In a number of cases, data important to quantitative analysis procedures are nonexistent or not measured with sufficient accuracy. Examples include the x-ray absorption parameter and the backscattering correction, R, especially at low beam energies. Conventional electron microprobes and scanning electron microscopes equipped with spectrometers are not suitable for such measurements, because the design constrains the analyst to a single value of the angle between the beam and the spectrometer axis.

During the past year, we have completed the construction of an electron/x-ray optical measurement bench which offers flexible control of the electron beam, electron gun, and specimen. This system consists of an electron gun and column, a specimen goniometer which is capable of three-axis orientation, and an x-ray spectrometer mount which can be used to measure x-ray intensities at x-ray emergence angles of 0 to 70 degrees, where the x-ray emergence angle is defined as the angle between the detector and the specimen surface. To achieve maximum flexibility in selecting experimental setups, the instrument was designed around a vertical axis of symmetry with the electron-beam forming system mounted horizontally. Around this vertical axis, the x-ray detectors have a freedom of movement that is limited only by the electron-gun subsystem. The specimen may also be rotated on this vertical axis, creating a range of beam incidence angles from 0-90 degrees. The combination of x-ray emergence and incidence angles allows for virtually every conceivable beam/specimen and tilt/x-ray emergence angle arrangement of interest.

In the initial experiments on the instrument, we have measured the absorption of x-rays as a function of x-ray emergence angle and compared the measurements to the existing literature expressions for x-ray absorption. From these measurements, we hope to develop a more accurate term for x-ray absorption which can be used in the quantitative analysis procedures for the electron probe.

8. Implementation of a Laboratory Accreditation Program (LAP) for the Analysis of Asbestos in Bulk Materials and in Air

E.B. Steel, S. Turner, J.D. Verkouteren, J.M. Phelps, M.D. Johansen, V. Wang, and R.A. Fletcher

Regulations by the Environmental Protection Agency and laws propagated by Congress have propelled asbestos abatement into a billion dollar a year industry. The need for standardizing the analytical methods that determine the need for abatement and compliance with state and federal regulations is critical. The two general areas requiring standardization are the analysis of bulk asbestos by polarized light microscopy (PLM) and the analysis of airborne asbestos in buildings by transmission electron microscopy (TEM). To address these needs, the Microanalysis Group has set up a National Reference Laboratory for Asbestos Analysis.

The new asbestos analysis laboratory includes new space, instrumentation, and personnel paid for initially by a Congressionally mandated program with EPA. The new instrumentation includes x-ray powder diffraction, light microscopy, and transmission electron microscopy (TEM) systems with computer and image analysis support. We have hired four new people with skills in polarized light microscopy, mineralogy, x-ray diffraction, crystallography, and transmission electron microscopy to develop and test standard measurement methods and reference characterize materials for asbestos analysis.

The asbestos research program has three main goals:

(1) Develop standard methods, materials, and laboratory technical requirements for a laboratory accreditation program for the analysis of asbestos in building materials;

(2) Determine methods of producing and characterizing air filter reference materials and quality assurance requirements for transmission electron microscopic analysis of asbestos on air filters; and

(3) Investigate air sampling methods for determining the concentration of asbestos in air for application to abatement clearance projects.

The Microanalysis Group is helping the National Voluntary Laboratory Accreditation Program (NVLAP) set up a laboratory accreditation program for bulk asbestos by developing four new bulk asbestos reference materials, by determining the accuracy of the polarized light microscope method for the analysis of asbestos, by developing and characterizing methods for the use of x-ray diffraction for the analysis of asbestos, by writing technical and quality assurance guidelines and requirements for laboratories applying for accreditation, by setting up a "model" laboratory in which the accreditation requirements and methods are tested, by characterizing a set of lab proficiency testing materials, by selecting and training a team of over 50 laboratory assessors for site visits to the labs. This accreditation program will include more than 500 laboratories.

A TEM accreditation program for the analysis of asbestos in air, including approximately 100 labs, will start next year. To prepare for this program, we have developed methods of preparing proficiency testing materials and run a round robin using these materials to test the main two steps in the measurement process, sample preparation and fiber counting and identification techniques. Reference materials are being designed and developed for use in calibrating identification techniques such as electron diffraction and energy dispersive x-ray analysis. Quality assurance and other technical requirements are being determined and realistically tested as we set up a "model" laboratory for the analysis of air filters. Other methods, such as scanning electron microscopy, are being investigated as alternatives or support techniques in the analysis of asbestos in air.

Since techniques used in sampling the air and preparing air filters are poorly defined in asbestos measurements, we are investigating the effects of various filter types, filter sampler designs, preparation methods, as well as the effects of transportation on the concentration and distribution of asbestos and other particles on the filter.

9. Molecular Compositional Mapping of Organic Compounds by Secondary Ion Mass Spectrometry

J.G. Gillen and D.S. Simons

Desorption of intact organic molecules by keV ion impact and subsequent mass spectrometric analysis of the sputtered secondary molecular ion flux has become one of the most widely used tools for analytical and structural studies of thermally labile organic molecules. The techniques and instrumentation developed for elemental ion imaging using Secondary Ion Mass Spectrometry (SIMS) are well established. We are attempting to extend these capabilities to the secondary ion imaging of molecular species.

A Cameca IMS-3f ion microscope was used for all organic SIMS studies. This instrument is equipped with a resistive anode encoder digital imaging system. Molecular ion images were acquired with 8 keV Ar^+ ion bombardment with typical primary ion current densities of 1-5 $\mu A/cm^2$. Model systems for imaging studies were prepared by evaporating the compound of interest from aqueous or ethanolic solution onto copper transmission electron microscopy grids. The presence of the deposited compound on the grid was confirmed by observation of characteristic parent and fragment ions in the mass spectrum. In all cases, molecular secondary ion images were generated using the parent molecular ion. Images with lateral resolutions of ~1 μm were obtained from a number of compounds including germicides, neurotransmitters, neurotoxins, organic dyes, alkaloids, surfactants, and amino acids. Collaborations with NIH have been initiated to study the capabilities of this technique for imaging organic compounds in biological tissue.

Another area of interest is the study of the fundamental interactions of energetic ions with molecular solids. In general, molecular species are very susceptible to primary ion beam induced structural degradation. It is generally assumed that these degradation processes will limit the desorption of intact molecules to the first few monolayers of the sample; subsurface molecules are thought to be fragmented by the penetrating ion beam well before they are exposed at the sputtered surface. Our results indicate that this is not the case. We have routinely been able to detect and image parent molecular ions after sputtering some tens to hundreds of nanometers into the sample. This suggests that molecular ion depth profiling is possible. The secondary ion signal of these initially buried molecules may be optimized by an appropriate choice of experimental parameters. For example, reduction of the primary ion energy by a factor of two increases parent molecular ion signals by orders of magnitude. Related studies that will be initiated include measurement of the sputter and secondary ion yields of organic molecules, the mechanisms by which compounds mixed in various matrices used in organic SIMS become more resistant to primary beam induced degradation, computer simulations of molecular sputtering, quantitative molecular analysis in solid materials, and the development of a general model describing damage production in ion bombarded molecular solids.

10. Compositional Mapping with a Camera-Based Imaging System on an Ion Microscope

D.E. Newbury and D.S. Bright

In the technique of compositional mapping, the microstructure of a specimen is revealed in computer-generated digital images in which the gray or color scale is determined by the actual concentrations of the various constituents and not by raw signal intensities. To achieve quantitative compositional mapping, it is necessary to carry out a complete quantitative elemental analysis at each point in an image. Rigorous corrections must be applied to the spectral data to account for all instrumental and physical effects on the measured radiation, just as would be the case for conventional quantitative analysis at a single location selected with a stationary beam. Digital compositional maps offer significant advantages over conventional qualitative area mapping methods, including realistic depiction of quantitative concentration information, greatly improved detection sensitivity, and flexibility for subsequent image analysis. Previous work in our laboratory has established compositional mapping for the electron probe microanalyzer.

Compositional mapping with secondary ion mass spectrometry (SIMS) carried out in the direct-imaging ion microscope offers several advantages over mapping with the electron microprobe: (1) the SIMS signal rate is of the order of MHz, so that images can be obtained in 10 seconds or less, even from trace constituents; (2) the high peak-to-background levels permit trace level imaging at the parts-per-million to parts-per-billion level; and (3) elements across the periodic table can be detected at high sensitivity, including H, Li, Be, B, and C.

To establish quantitative compositional mapping with ion images, a measurement technique has been developed which relates the signals measured with the imaging detector system to signals measured with the conventional pulse-counting multiplier detector as the reference. The imaging detector consists of secondary ion-to-electron conversion at a two-stage channel plate, electron-to-photon conversion at a transmission scintillator, photon-to-electrical signal conversion at a charge-coupled device TV camera, and digitization of the electrical signal with an 8-bit analog-to-digital converter into a 512 x 512 image array. Comparison of the signals measured on pure elements and homogeneous alloys with the two detectors reveals that the response of the imaging detector depends strongly on the ionic species being measured. Quantitative image measurements require the use of calibration curves to convert the image signal at each picture element to the equivalent multiplier count. Compositional maps are then prepared by using sensitivity factors measured on known alloys with the multiplier detector to convert the image intensities to equivalent concentrations.

The SIMS compositional mapping technique has been applied to the characterization of chemical microstructures in aluminum-lithium alloys and to high transition temperature (Tc) superconductors. Microstructural features observed in Al-Li include second-phase particles, grain boundary segregation and denudement, and surface segregation. In bulk, high Tc superconductors, complex microstructures are observed which include extensive segregation of a variety of chemical phases on a scale of 1 to 10 micrometers.

11. Concentration - Concentration Histograms: Scatter Diagrams Applied to Quantitative Compositional Maps

D.S. Bright, D.E. Newbury and R.B. Marinenko

Compositional mapping with the electron microprobe requires standardization of, and instrumental and matrix corrections to, the raw x-ray data to achieve a quantitative elemental analysis at each pixel location in a map. The resulting arrays of compositional values are then displayed on a cathode ray tube as images with selected gray or color scales to encode the range of compositional values. Often it is of interest to establish the spatial correlation of two or more constituents. Such correlations can be conveniently presented in visual form by the use of the well-known technique of primary color overlay, whereby two or three "single band" (or single constituent) images are overlaid with the red, green, and blue guns of a color CRT. By the laws of color addition, the appearance of secondary colors in the image field reveals regions of spatial overlap of any two constituents. While this is a powerful and widely used technique, it suffers from the deficiency that it is difficult to visualize the compositional ranges of the single band images in a meaningful way in the final color composite image. As an alternative, we have developed the concentration-concentration histogram (CCH), which provides a visual display of the numerical relationships of the constituents and promises to be useful for diagnosing experimental problems and evaluating data.

Histograms of images are often obtained by scaling the images to cover a concentration range of 0 - 255, and then accumulating the intensities of each pixel in a one-dimensional array of 256 bins in the usual manner. The concentration-concentration histogram is a two-dimensional analog of this, and is a type of scatter diagram. Each pixel in one image, A(x,y), representing element A at coordinates (x,y), is associated with the corresponding pixel in the other image B(x,y). The concentrations represented at this location are accumulated in a 256 x 256 pixel array CCH, where the abscissa of the CCH corresponds to the concentration of A and the ordinate to the concentration of B. The accumulated number in each pixel in the CCH can be displayed with selected gray or color scales to represent the CCH as an image. Such a visual display of the CCH allows the analyst to recognize quickly and quantitatively those compositional value pairs which occur commonly in the original single band images. The CCH often shows intense spots where most of the pixel pairs tend to clump, along with some points or bins of very low intensity representing only one or two pixel pairs for the original quantitative maps. We have found the scattered low intensity points to be as important as the clumps. To visualize these low intensity points as well as the high intensity clumps, the accumulated number in each pixel in the CCH can be displayed by means of a scale which presents the wide dynamic range of the data to an observer. A "thermal color scale" is especially effective for this application.

A powerful aspect of the CCH is the "trace back" capability to highlight selected spatial compositional features in the original images according to concentration features recognized in the CCH. Once a feature of interest in the CCH has been identified, the procedure is reversed to identify the specific pixel locations in the original compositional maps which correspond to selected concentration-concentration conditions. This combination provides a powerful tool for the characterization of chemical microstructures.

12. Compositional Mapping by Electron Probe Microanalysis of Bulk and Thin-Film Superconductors

R.B. Marinenko, D.E. Newbury, B.B. Thorne, E.B. Steel, and J.D. Verkouteren

Compositional maps are prepared by digitally stepping the electron beam of the electron probe microanalyzer (EPMA) in a predefined array on the surface of the specimen. At each point in the array, x-rays from the elements of interest are accumulated for a preselected time period, using wavelength dispersive (WDS) and/or energy dispersive (EDS) spectrometers. With combined WDS/EDS spectrometry, as many as ten elements can be mapped simultaneously. Each pixel in the resulting map is corrected for dead-time, background, and when necessary, for spectrometer defocussing. The concentration of each element is calculated at each pixel with complete correction for matrix effects. The result is a map of quantitative elemental distributions which can be displayed on a gray scale or in color on an image analysis system. This mapping technique is ideal for studying regions from about 20 μm to 1 cm along an edge. Map sizes can be 64 x 64, 128 x 128, or 256 x 256 pixels.

Compositional mapping has been used in our laboratory to study bulk and thin-film specimens of the 1-2-3 Yttrium-Barium-Copper high-temperature superconductors which are being produced in NIST laboratories. The bulk materials are prepared from intimate mixtures of the oxide powders which are subjected to a series of mixing, pressing, grinding, sintering, and annealing steps. Thin films are prepared by RF sputtering or thermal evaporation of the oxides onto a substrate, which initially produces a homogeneous material that must be subsequently annealed in oxygen to produce the high Tc state. The resulting product is dependent upon the experimental conditions used in preparation. Physical properties, such as the critical current density, magnetic susceptibility, brittleness, and sharpness of the superconducting temperature transition are related to the microstructure. Quantitative compositional mapping is providing a valuable link to correlate and understand the processing procedures and the resulting physical properties. In addition, reactions between the melt and the crucible walls have been studied in depth.

Maps of bulk specimens have shown that these superconductor materials are inhomogeneous and porous. The superconductor phase, which has a composition of $YBa_2Cu_3O_{7-x}$, is usually observed in conjunction with other phases that have been identified as BaY_2CuO_5 (called the "green" phase) and a combination of CuO_2 and $BaCuO_2$. The presence of these phases has not been attributed to unreacted material since the grain size is five times larger than the starting material; rather, their presence has been attributed to unexpected melting, during sintering, which results in segregation. The pores are believed to be an asset in the production of the superconductor phase as they allow excess oxygen needed in the formation of this phase to enter the specimen during sintering. The RF sputtered films, which are about 1 μm thick, have also been shown to become inhomogeneous after annealing.

Recently, we have begun to study a new type of high-Tc superconductor, 1-1-1-2 Bi-Sr-Cu-Ca oxides, which is in the form of thin films. Laser ablation is used in the production of these films. Because there are more than three elements of interest, EDS mapping has been used. Initial studies have shown that these films are more homogeneous than earlier preparations of other high-Tc superconductors.

13. Fundamental Studies of Matrix Correction Models for Quantitative Electron Probe Microanalysis

K.F.J. Heinrich

The accuracy of quantitative electron probe microanalysis has not significantly improved in the last decade and is below the levels thought to be achievable. Although several parameters of significance have not been fully characterized as yet, work by competent investigators has diminished. Most present users depend on the instrument manufacturers for the installation of data reduction software. Presently used routines are quite complex and involve many parameters; users rarely specify all pertinent parameters, and therefore, statements concerning accuracy of methods are at best of limited usefulness. In particular, claims of improvements in fundamental approaches must be considered doubtful when the methods used to prove them are not fully specified. To further complicate this situation, the databanks on relative intensities obtained from binaries which are used to prove such claims, are tainted by the inclusion of imprecise measurements, some taken before accurate detector systems were available. It is quite typical that such claims are not supported by the application of the proposed method by other operators.

We have therefore begun the following efforts to increase accuracy in PMA by the classical model (normal beam incidence upon a thick uniform specimen):

> Use, in a menu-type program, a set of carefully purged data from which old or not self-consistent groups of data will be eliminated "a priori". The menu will permit switching values of parameters and algorithms for various correction aspects, including the newest proposals of parameters and methods.
>
> Use only those experimental data for the evaluation of each aspect of correction (absorption, fluorescence, etc.) which depend significantly upon the choice of models and parameters. Therefore, the random spread of the results will be reduced.
>
> Propose improved models and investigate uncertain parameters after evaluating and comparing several sets of parameters and models, including the Monte Carlo technique. We will then use the Monte Carlo method to investigate ways in which less traditional configurations (inclined electron beam, thin films, layered specimens, fibers, and submicron particles) can be used quantitatively with increased accuracy.

To make the comparison of approaches more objective, we will propose a minimum set of data that must be given to fully characterize the process. Based on our overall results, we will also propose the best methods for use by instrument manufacturers in their software programs.

14. Raman Microprobe Spectroscopy Applied to the Characterization of Superconducting Materials

E.S. Etz, T.D. Schroeder, and F.S. Pereles

The photon spectra of superconductor materials are of interest as they provide fundamental information on structure-property relationships. Hence, Raman spectroscopy has come to play a central role in the characterization of high-Tc superconductor materials. The technique provides a sensitive probe of both the phonon structure of the superconductor and of impurity phases in these materials. Numerous reports, principally from studies of bulk samples, on the Raman spectra of these materials have appeared, and the literature is well developed with respect to the interpretation of these results. The spectra provide diagnostic information on structure, bonding, and symmetry, as well as the dynamics of structural phase changes. Micro-Raman spectroscopy extends these investigations into the realm of microscopic dimensions to complement other (i.e., elemental) microprobe techniques for spatially resolved mapping of compositionally different domains. We have applied the NBS-developed scanning Raman microprobe (with photon counting detection) principally to the study of several types of samples in the yttrium-barium-copper-oxygen (Y-Ba-Cu-O) system. These are among the first few micro-Raman studies reported to date. The goal is to provide microstructural characterization with a spatial resolution of a few micrometers, specifically with regard to crystal structures and phase relationships, compositional homogeneity, and oxygen stoichiometry. These findings are examined with reference to various methods of preparation, processing, and heat treatment, and are correlated with the physical properties determining superconductivity. In the Y-Ba-Cu-O system, the samples examined are polycrystalline ceramic powders, sintered pellets, and single-crystal material, all of the 1-2-3 composition $Y_1Ba_2Cu_3O_{7-x}$, with x varying between 0 and 1, the range over which this system is known to lose its superconducting properties, and the crystal symmetry changes from orthorhombic to tetragonal in this transition. The samples examined have all been prepared and extensively characterized by other methods (e.g., x-ray diffraction, magnetic susceptibilty and resistance measurements) in investigations by collaborators of the Ceramics Division of NIST. In the micro-Raman measurements of these samples, we have obtained analytically useful room-temperature spectra of the principal phases in this system with the intent to identify also the relevant parasitic phases of composition Y_2BaCuO_5, $Y_2Cu_2O_5$, $BaCuO_2$, and Cu_2O. These results show that micro-Raman spectroscopy can provide unique information on the identity of distinct microscopic phases not revealed by bulk methods of structure determination. Overall, the spectra indicate a compositional heterogeneity which, at the same microscopic level, has also been revealed by electron probe microanalysis. We are also applying the Raman microprobe with multichannel detection (PARC OMA-3 with intensified diode array) to the study of these samples to elucidate the multiplex advantage in the acquisition of the spectra of these weakly scattering solids. Work in progress focuses on some of the newer compositions of superconductors. As part of our research program to provide analytical support to other NIST groups in the full characterization of these materials, future investigations will focus on the study of precursor species of significance to several methods of synthesis, and the environmental degradation of these samples due to their sensitivity to moisture.

15. XRF Analysis of SRM 2704 (Buffalo River Sediment) by Automated Borate Fusion

Z. Wang and P.A. Pella

A new SRM 2704 (Buffalo River Sediment) was analyzed in the past year by several methods in the Center for Analytical Chemistry including x-ray Spectrometry. All measurements leading to the certification of this material were coordinated through M.S. Epstein of the Inorganic Analytical Research Division. Eight samples were submitted for the XRF determination of the elemental homogeneity and quantitative analysis of twelve elements. A loss-on-ignition of 9.3% was determined by heating several samples to 1050 °C in a muffle furnace. Duplicate samples of 1.100 g each were fused with 6.000 g of lithium tetraborate in an automated fusion apparatus in platinum-gold crucibles at 1050 °C and the resultant homogeneous solution as fused glassy disks were ground and polished on one side prior to measurement. For determination of inhomogeneity, a total of 16 fused specimens were measured for Al, Si, P, K, Ca, Ti, Mn, Fe, Zn, Sr, Rb, and Zr. Nine fused specimens were measured for elemental composition. The computer program NBSGSC was used to correct for interelement x-ray absorption effects. Standard samples were prepared from compounds better than 99.95% pure, such as oxides or carbonates.

Analysis of XRF intensity data for sixteen specimens showed no statistically significant differences in the elemental composition of this material. The XRF results of the quantitative analyses of this material for certain key elements such as Al, Si, P, K, Ca, Ti, Mn, and Fe were found to be in excellent agreement with the certified values. In addition, four SRMs were analyzed concurrently with SRM 2704 quality assurance samples and analyzed.

16. Total Reflection XRF Analysis with a Rotating Anode Source - Some Preliminary Observations

P.A. Pella and R.C. Dobbyns (IMSE)

Energy-dispersive x-ray fluorescence spectrometry (EDXRF) is a widely used analytical technique because it is non-destructive, rapid, and capable of multi-element analysis. However, a major drawback is its relatively low sensitivity for trace analysis when compared to other trace element techniques such as neutron activation and ICP. To improve (i.e., lower) the minimum detection limit (mdl) in EDXRF, techniques to enhance the signal relative to the background need to be developed. This can be accomplished through the use of bright x-ray sources such as synchrotron radiation or by a rotating anode source, both of which are well suited for use with reflection geometry to reduce the background contribution.

Previously, we demonstrated sensitivity (mdl) below 1 ppb for selenium in SRM 1643b Trace Elements in Water and analyzed SRM 1598 Bovine Serum for selenium at the 42 ppb level. This work was published in 1988 this year in **Anal. Chem.** and described analyses using monochromatic, energy tunable, synchrotron radiation in a total reflection mode. We plan to continue our work using synchrotron radiation during the next year and to investigate the potential of the high flux white beam for trace analysis.

One alternative to synchrotron radiation is a high intensity commercial rotating anode source which can also be used in the total reflection geometry for trace analysis. Although substitution of a rotating anode source for synchrotron radiation will result in somewhat poorer detection limits, there are several advantages to be gained with a laboratory based system such as convenience and access. Much of our work this year was directed to the fabrication of an in-house total reflection spectrometer. A double-crystal spectrometer was purchased for this purpose to interface with a rotating anode source. Additional instrumentation was designed and constructed for orienting the x-ray detector with respect to the analyte sample. A tube was built so that the path from the exit of the source to the entrance window of the double crystal spectrometer is vacuum tight to allow either a reduced pressure or a Helium path. The double-crystal spectrometer functions as a means to provide some tunability of x-ray beam energy and size, and to control and maintain the required substrate reflector critical angles relative to the x-ray beam. Preliminary measurements have been performed with this system using a focused x-ray beam to characterize the topography of some metallurgical surfaces.

We now plan to determine minimum detection limits for selected elements using this system and make a relative comparison of its sensitivity to the synchrotron source system in the total reflection geometry. Several types of optically flat substrates will also be characterized in an effort to obtain chemically pure substrates to minimize the chemical blank.

17. Development of Immobilized Chelator Membranes for Preconcentration of Trace Elements

P.A. Pella and Z. Wang

Increase in sensitivity of x-ray analysis by pretreatment of the sample prior to analysis has long been recognized as an important goal in this field. We have developed several techniques during the past ten years for preconcentration of samples to permit quantitative x-ray analysis at ppb levels, especially for liquid samples where as much as one liter can be preconcentrated. These techniques have basically involved the prior separation of the trace elements (usually transition elements) from the major constituents using column chromatography. The trace elements can then be concentrated on paper filters impregnated with ion-exchange resins. The recent availability of commercial ion-exchange resins dispersed in thin films of porous Teflon should spark a renewed interest in this technique.

To decrease the sample preparation time by eliminating the need for prior removal of major sample constituents requires that thin substrates be developed that are much more selective than the ion-exchangers. For this reason, we have developed substrates from cellulose fibers to which we have attached covalently bound chelating groups such as dithiocarbamate or oxine (8-hydroxyquinoline). We have prepared derivatized filters from several grades of commercial filters of different thickness and evaluated their performance with regard to analytically useful capacity, mean exchange rate, and suitability for trace element preconcentration.

For purposes of evaluating trace element recoveries, we chose to analyze Fe, Cu, Zn, and Cd in NIST/SRM 1566 Oyster Tissue. The tissue samples were first treated with nitric acid in a microwave oven followed by treatment with perchloric acid to ensure complete decomposition of organic material. The residue was dissolved in acetate buffer at pH 6.0 and the solution pumped through a filter for a fixed time to collect the trace elements. The calibration curves prepared using standard aqueous solutions of the trace elements demonstrated good linearity and reproducibility of recoveries up to at least 500 micrograms of element per filter. However, we found variable recoveries when the NIST/SRM Oyster Tissue was analyzed. We found that the elemental capacity of these derivatized filters varied considerably, e.g., sometimes by as much as a factor of two. We believe this has a marked influence on the recoveries of the trace elements in the Oyster Tissue.

In an effort to overcome the variability of the elemental capacity of the filters, preliminary work has been performed to prepare derivatized paper pulp from which sheets of appropriate size can be fabricated. This procedure should result in filters of more uniform and reproducible elemental capacity. We are working closely with the NIST Fibrous Systems Division to develop an improved derivatized filter and expect to evaluate its performance during the coming year.

18. Preparation and Verification by Electron Capture Detection of Primary Gravimetric Standards of Volatile Toxic Organic Compounds (VTOC's) at the 15-500 Parts-Per-Trillion Level

G.C. Rhoderick

The program to prepare standards of VTOC's for EPA to use in the programs to monitor hazardous waste sites and incinerator burns has been in existence for many years. Until now, all of the mixtures prepared were at the ppm and ppb levels, but recent needs have required us to push our standards generation capabilities at least an order of magnitude lower in concentration.

Gravimetric standards containing halogenated toxic organic compounds were prepared at the 15-500 ppt level. These standards were blended using the NIST microgravimetric procedure for volatile organic compounds. Compounds in these mixtures include bromomethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane (methyl chloroform), trichloroethylene, carbon tetrachloride, tetrachloroethylene, 1,2-dibromoethane and trichlorofluoromethane (CFC-11). Initially, standards were prepared at the 10 and 100 ppb levels and then ppt level standards were made by transferring a precalculated amount of gas from these standards to new cylinders and adding nitrogen to the appropriate pressure. These standards are at very low levels and contamination could easily take place in the preparation procedure and the system. Therefore, the pure organic reagents were analyzed to quantify impurities. The matrix nitrogen was also carefully analyzed and impurities were quantified. The set of standards were analyzed on a gas chromatograph equipped with an electron capture detector. The data were then plotted using the area counts versus the gravimetric concentration for each individual compound and the predicted concentrations were determined by a quadratic equation. The results showed good agreement between the gravimetric concentrations and those predicted from the curve fit which confirmed the internal consistency of the set of standards. The absolute average of the residuals (predicted minus gravimetric concentration) for a given organic compound in the set of standards was 2 ppt maximum which is considered excellent at this concentration level.

The standards have been used to certify mixtures containing these compounds for several research groups. They have also been used to certify mixtures of toxic organic compounds for the State of California Air Resources Board for use in their air quality programs.

19. Developed and Certification of the First SRM Containing ppb Levels of Multiple Volatile Toxic Organic Compounds

W.L. Zielinski, Jr., G.C. Rhoderick, and W.R. Miller

Analyses of ambient air samples for volatile toxic organic compounds in the low ppb range are routinely conducted using GC and GC/MS systems that previously have been calibrated with appropriate gas standards. Such calibrations are tedious and prone to calibration errors when several standards must be used to cover a sufficient number of organic compounds. In an attempt to relieve this situation, research has been conducted at NIST over the past several years to assess the feasibility of developing a gas standard containing a substantial number of these compounds. This research has led to the refinement of preparative and analytical techniques that has resulted in the development of stable gas standards containing as many as 18 volatile toxic organic compounds in the low ppb range in the same gas cylinder, and to the issuance of a Research Material (RM) representing a limited number of cylinders containing a seven-component mixture at 5 ppb (RM 8511). The compounds in the 18 component mixture are:

Benzene
Bromomethane
1,3-Butadiene
Carbon tetrachloride
Chlorobenzene
Chloroform
1,2-Dibromoethane
1,2-Dichloroethane
Dichloromethane
1,2-Dichloropropane
Ethylbenzene
Tetrachloroethylene
Toluene
1,1,1-Trichloroethane
Trichloroethylene
Trichlorofluoromethane
Vinyl Chloride
o-Xylene

The stability of the gases has been determined over a several month time period. Only 1,3-butadiene exhibits questionable stability. Plans currently are underway for the development of the first NIST Standard Reference Material (SRM) of a multicomponent mixture of volatile toxic organic compounds at the low ppb level. This SRM will contain 18 pure compounds, each at a nominal concentration of 5 ppb by mole in a high-purity nitrogen matrix gas. The concentrations will be certified by intercomparative gas chromatographic analysis against absolute gas standards that are prepared by NIST using a microgravimetric procedure. The 1,3-butadiene stability question will have to be resolved before this gas can be certified in the mixture.

Based on extensive research and experiences with numerous gas standards containing the other 17 components and related compounds in the mid to low ppb range, it is anticipated that the uncertainty of the certified concentrations in this SRM will probably be on the order of 10% relative at the 95% confidence level with a stability of several years. A contract has been let for the commercial preparation of a lot of 20 cylinders containing mixture in accordance with NIST technical specifications. Several state and Federal agencies have already expressed interest in acquiring this SRM, which should be available from the NIST Office of Standard Reference Materials by the summer of 1989.

20. Development and Application of Coulometric Titration as a Direct Measurement of CO_2 Compressed Gas Cylinder Mixtures

G.D. Mitchell

Coulometry has been established as an important and reliable method for the determination of sulfur oxides and other electroactive compounds, especially at low concentrations. It is capable of producing analytical results of very high precision and accuracy. A constant flow coulometric titration system for the analysis of SO_2 has been developed, exhaustively characterized and described in previous reports. The system was designed and evaluated to determine that 1) the electrode reaction proceeds at a high current efficiency; 2) no analyte species escapes analysis and no electroactive species enters the analytical compartment; and 3) the end-point indicator is of high precision and accuracy. The system was slightly modified for the analysis of CO_2 and consists of a dual compartment electrochemical cell, a semi-aqueous absorption solution and electrolyte, an optical end-point detection system, a silver anode and platinum cathodes, and an accurate and precise flow control system. One application of the system was in the atmospheric CO_2 standards program. At present the reference method for the analysis of atmospheric CO_2 standards is non-dispersive infrared spectrometry (NDIR) using gravimetrically prepared reference standards as calibrants. Selected CO_2 mixtures were analyzed using the coulometric system to evaluate whether a bias existed in the reference standards. This was done as part of our program to verify our standards by at least two methods. The analysis of one particular mixture by coulometry showed it to be 341.7±1.7 ppm CO_2 while the value from gravimetry was 342.0±0.4 ppm. Within the analytical uncertainties, both methods give the same value.

The coulometric system was then tested to determine a lower detection level. Preliminary results showed that without any further modifications, the lower level was about 1 ppm with a 3:1 signal to noise ratio. The upper limit has not been established but will be dependent on the absorption capacity of the reactant solution calculations indicate that it can be as high as 7%. The system has not been evaluated for response to interfering gas species; therefore, it is presently being used to evaluate only cylinder gas mixtures.

21. Development of Isotope Dilution Mass Spectrometry for Absolute Determination of Carbon Dioxide Abundance in Air

R.M. Verkouteren

Cooperation between the Gas Metrology and Mass Spectrometry Groups in the Center for Analytical Chemistry has led to the development of an absolute method for the determination of the abundance of CO_2 in air at levels of 300-400 ppmv. The method utilizes high-precision manometry and isotope dilution mass spectrometry (IDMS).

In this method, an aliquot of air is precisely measured and equilibrated with a precisely measured amount of C-13 depleted (spike) CO_2. The isotopically altered mixture of CO_2 is then isolated from the air and measured, by mass spectrometry, to quantify the extent of isotopic alteration. The concentration (in ppmv) of CO_2 in the original air can be calculated using the formula:

$$C_{CO_2} \cdot 10^{-6} = \frac{P_{spk}}{P_{air}} \cdot \frac{V_{spk}}{V_{air}} \cdot \frac{T_{air}}{T_{spk}} \cdot \frac{Z_{air}}{Z_{CO_2}} \cdot \left[\frac{F_{mix} - F_{spk}}{F_{air} - F_{mix}} \right]$$

where the factors are ratios of pressure, volume, temperature and compressibility between the spike and air; the bracketed term is the ratio of differences in isotopic fractional abundances (F) between the CO_2 of the air, spike and mixture.

The gas mixing system consists of two electropolished and chemically passivated stainless steel volumes, the ratio of which was determined by gas expansion methods. Air and spike CO_2 are measured in these volumes and then mixed through a pump-driven recirculating loop. Subsequently, the CO_2 mixture is frozen out nearly quantitatively in a liquid argon cold trap. Isotopic compositions of carbon dioxide are determined using a mass spectrometer designed and constructed at the NIST. The instrument is a 30 cm radius, 90° deflection magnetic sector mass spectrometer with extended flight path geometry and a triple, deep-Faraday-cup collector.

The goal for absolute uncertainty at the 95% confidence level was set at 0.1% with an analytical imprecision at that level or better. Propagation of uncertainties in all accountable variables (e.g., ratios of pressure, temperature, volume and isotopic composition) leads to an estimation of total absolute uncertainty of 0.13%. Carbon dioxide abundance values generated by IDMS compare favorably with those of gravimetry, the definitive method at present for SRM certification. For a particular sample of real air, IDMS gives 347.43 ± 0.45 ppm while gravimetry gives 347.6 ± 0.4 ppm. Analytical imprecision of replicate analyses via IDMS is also quite satisfactory: 0.11%.

It is planned to measure a series of CO_2 samples at different concentrations, to refine further the measurement methodology, and to explore the possibility of applying the system to other gaseous components of our atmosphere.

22. Development of a Low-Level Nitric Acid Generator

L.J. Nunnermacker, R.R. Dickerson (University of Maryland), and W.D. Dorko

A calibration source has been developed and characterized, which can be used to generate HNO_3 concentrations in the parts-per-million by volume (ppmv) and sub-ppmv range with verifiable accuracy. The reaction which occurs is:

$$HCl_{(g)} + AgNO_{3(s)} \longrightarrow HNO_{3(g)} + AgCl_{(s)} \quad \Delta G^{o} = 13.3 \text{ kcal mol}^{-1}.$$

Nitric acid was generated by passing a gaseous mixture of HCl in N_2 (in this instance a nominal value of 93 ppmv) through a 145 mm length of 4.0 mm I.D. teflon tubing containing 6.21 g (~6-8 mesh) of crystalline silver nitrate. The concentration of the HCl mixture was found to be 94.3 ppmv ±2.1 (as measured by ion chromatography (IC)) and was stable over a period of two and a half years. The flow of HCl was maintained by a 0.5 L min^{-1} mass flow controller (MFC) with Kalrez O-rings to minimize corrosion and a low flow of nitrogen was passed through the flow controller (when the HCl was not used) to keep the flow controller dry and prevent corrosion. Lower HNO_3 concentrations (< 87 ppmv) were obtained by dynamically diluting the flow from the generator with "zero air". Background concentrations of HNO_3 were determined by replacing the HCl flow with an equivalent flow of nitrogen or zero air over the $AgNO_3$ column. All connections, solenoid valves, and tubing in the system were TFE teflon unless otherwise specified.

The effluent of the $AgNO_3$ column was tested for HNO_3, using three independent techniques: chemiluminescent detection (CD), ion chromatography (IC), and tunable diode laser absorption spectroscopy (TDLAS). At a column temperature of 20 °C, the three distinctly different measurements of HNO_3 ($[HNO_3]_{CD} = 85.2 \pm 2.6$ ppmv, $[HNO_3]_{IC} = 79.6 \pm 6.1$ ppmv, $[HNO_3]_{TDLAS} = 76.9 \pm 6.7$ ppmv) agree within the estimated accuracies of each technique. Dilution of the column effluent produced concentrations of HNO_3 at lower levels and was linear from 0.01 to 87.4 ppmv (as determined by CD) indicating good mixing and negligible surface adsorption of nitric acid. The CD technique was used on a daily or weekly basis to check the output of the generation system over a period of three months. The HNO_3 produced during this time was remarkably stable and no change in efficiency was observed.

The $[HNO_3]$ ultimately depends on the [HCl] and thus, the flow rate of the HCl could be an important factor. However, this system demonstrates very little HCl flow dependence in the range of 100 to 500 cm^3 min^{-1}, and produced 3.6% less HNO_3 at the lower flow rate. Additionally, the system was relatively insensitive to temperature changes and the $[HNO_3]$ increased by only 4% from 20 to 70 °C.

23. Characterization of the Output of a Nitric Acid Generation System Using Tunable Diode Laser Spectrometry and Chemiluminescence Detection

L.J. Nunnermacker and R.L. Sams

A new calibration source of gaseous nitric acid has been developed, based on the conversion of gaseous hydrogen chloride to HNO_3 on solid silver nitrate. A description of the generation system is given in the previous report. Here we will describe the analytical efforts to characterize the generator output.

Three different analytical techniques were used to quantify the HNO_3 content of the generator: chemiluminescence detection (CD), tunable diode laser absorption spectroscopy (TDLAS), and ion chromatography (IC). Fluorescence of NO_2 is the heart of the commercially available CD system. First, all NO_y's are converted to NO by passing the gas over a hot stainless steel substrate, then the NO is converted to excited NO_2 by a reaction with ozone. The excited NO_2 then fluoresces which is detected by a photomultiplier tube and recorded on a strip chart recorder. TDLAS relies on the highly sensitive technique of second derivative absorption spectroscopy. The diodes emit very narrow band infrared radiation which is detected after passing through the gas of interest. Each gas has a unique infrared spectrum which leads to a very selective and sensitive method of molecule detection. When the absorption cross section of a rotation vibration line is known, the concentration of the molecule can be determined. In IC, the sample gas is bubbled through an absorbing solution after which aliquants of the solution are injected into an IC to effect the separation and then detection of Cl^-. The IC is calibrated with a chloride salt solution for quantification. The final concentration of 80.6 ppmv HNO_3 was measured using these three different techniques. With the conversion column operating at 20 °C the HNO_3 concentrations measured by the three different methods were as follows: $[HNO_3]_{CD} = 85.20 \pm 2.6$ ppmv, $[HNO_3]_{TDLAS} = 76.9 \pm 6.7$ ppmv, and $[HNO_3]_{IC} = 79.6 \pm 6.1$ ppmv (uncertainties are 1σ). The effluent of the $AgNO_3$ column was also tested for residual HCl, in the form of chloride ion (Cl^-), but no Cl^- was detected using IC. Other oxides of nitrogen tested included NO, NO_2, and HONO. The HNO_3 gas was >96% pure containing <2.5% HONO (estimated maximum) and 1.2% NO_2 as determined by TDLAS, and <0.1% NO as determined by CD.

Although IC and TDLAS are more specific techniques for measuring HNO_3, both techniques require much sample preparation and analysis time. CD, as mentioned above, is commercially available and easy to use. Nitric acid is measured using CD by alternating the sample flow through a nylon filter or bypassing the filter. The difference in the two signals is HNO_3 (or other acidic gases including HONO and HNO_4). Because this method was the most non-specific of the three, it delivered the highest (85.2 ppmv) concentration of HNO_3. The TDLAS system was then used to confirm that, indeed, HNO_3 was being generated and to quantify the concentration using the ro-vibration line at 1722.4390 cm^{-1} in the ν_2 band of HNO_3. The relative precision of the absorption measurements was ±2.6 ppmv, however, other factors such as reproducibility between runs and the knowledge of the absolute cross section increased the uncertainty to ±6.1 ppmv at 76.9 ppmv. The $[HNO_3]$ determined by TDLAS was definitely a lower bound, since most of the errors would tend to decrease the observed concentration (losses to the White cell's walls and possible laser broadening of the line).

24. Study of the Chemistry of $NO_2/HNO_3/H_2O$ in Compressed Gas Cylinder Mixtures

B.C. Cadoff, W.D. Dorko and J.E. Suddueth

Our interest in the study of the chemistry, kinetics and equilibria of compressed gas mixtures containing NO_2, HNO_3 and H_2O stems from the fact that virtually all cylinders containing NO_2 in air, from the low to the high ppm levels, are actually NO_x mixtures containing both NO_2 and HNO_3. The concentration levels of HNO_3 have been quite variable, ranging from less than 1% to approximately 50% of the NO_x value. Different cylinder mixtures exhibit different behavior. Some cylinders, after standing unused for months, will yield a higher HNO_3 level when first analyzed; and, with continued sampling over a period of an hour, the HNO_3 level will drop to a constant level. However, the total NO_x level will remain constant from the beginning. Other cylinders will show constant HNO_3 and NO_2 concentrations throughout the analyses.

For many analytical purposes, a constant composition NO_x cylinder is quite acceptable, and generally we have found these cylinders to be stable in NO_x concentration over a period of at least a year. One of the analytical methods used in this laboratory, as well as many other laboratories is the chemiluminescent detector equipped with a high temperature converter which quantitatively reduces the higher oxides of nitrogen, such as NO_2 and HNO_3, to NO. The NO thus produced reacts with O_3 to give the characteristic chemiluminescence which is detected by the phototube in the analytical instrument. When used in this type instrument, a cylinder can contain varying levels of NO_2 and HNO_3 and still be a useful calibration standard.

However, there is also an interest in cylinders that contain either pure NO_2 or pure HNO_3. We are now trying to produce pure HNO_3 in cylinders and the known chemistry of the nitrogen oxides suggests that this may be possible.

In the absence of light, the following reactions take place.

$$O_2 + 2NO \rightarrow 2NO_2 \quad (1)$$

$$3NO_2 + H_2O = 2HNO_3 + NO \quad (2)$$

$$2NO_2 = N_2O_4 \quad (3)$$

$$NO + NO_2 = N_2O_3 \quad (4)$$

$$NO + NO_2 + H_2O = 2HNO_2 \quad (5)$$

Reaction (1) goes to completion and is a rapid reaction, especially in NO_2 cylinders which contain air (21% O_2). The other reactions are equilibria for which the rate constants are not available. Reaction (2) is especially interesting since this is the reaction that produces HNO_3; it also forms NO, which would be expected to react rapidly with the O_2 present to form NO_2. Thus, we predict that this reaction would go to completion as follows:

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3 \quad (6)$$

This reaction also shows that for each NO_2 that reacts, an equivalent HNO_3 is formed, which would explain the observed constant NO_x composition of these cylinders. Note too, that in the presence of O_2, the above reactions predict the presence of only NO_2, HNO_3 and H_2O.

We have performed experiments in which we have introduced a H_2O vapor in nitrogen mixture into cylinders of NO_2. In the first experiments with 1000 ppm NO_2 cylinders, we have observed expected dilution of the NO_x, due to the addition of the wet nitrogen, and an increase in HNO_3 amounting to about half the expected increase based on reaction (6) after a period of several days. These experiments will continue and the cylinders will be examined periodically over a period of several months to note any changes in NO_2 and HNO_3 concentrations.

25. Development and Characterization of a Low Concentration H_2O_2 Generation System

R.L. Sams, B.C. Cadoff, and W.D. Dorko

Hydrogen peroxide has been shown to be a significant atmospheric reactant in the chemical transformations leading to acid rain. In particular, H_2O_2, which oxidizes SO_2, is now regarded as an important contributor to the ultimate H_2SO_4 concentration in the atmosphere. We have begun a program, supported by EPA, to generate and analyze mixtures of H_2O_2 at the low ppb level to assess atmospheric H_2O_2 concentrations.

The generation of ppb levels of H_2O_2 has been reported by several workers and involves either flowing air directly over a solution of H_2O_2 or more usually, flowing air through a permeable tube through which H_2O_2 enters from the surrounding solution. The concentration of H_2O_2 generated follows Henry's law and the concentration appears to be stable, provided the temperature of the H_2O_2 solution is kept constant and the solution concentration does not change. The output of such a generator could be analyzed directly, and linearity of concentration with flow rate could be confirmed by successive dilutions down to the desired ppb level.

The method to be used for the relative measurement of different concentrations of H_2O_2 involves the use of the tunable diode laser absorption system (TDLAS): hydrogen peroxide generated by one of the appropriate techniques described above will be diluted with dry nitrogen and passed through a White cell at a reasonable flow rate keeping the White cell at a total pressure of about 10 torr. A strong absorption line from the strongest infrared band ν_6 at 1265 cm^{-1} will be used to monitor the H_2O_2 concentration. Second derivative spectroscopy will be employed in conjunction with sweep averaging to use the most sensitive detection available. The minimum detection when using this method is usually sub-parts-per-billion by volume if reasonably strong absorption lines (1-10 $atom^{-1}cm^{-2}$) are used.

An independent measure of the concentration of H_2O_2 can be performed in the following way. A sample of high concentration hydrogen peroxide in water will be passed through a short cell at known pressures. Lines of both H_2O_2 and H_2O will be measured using TDLAS. The partial pressure of H_2O will be determined and the line strength of the H_2O_2 calculated as follows: three series of 10000 averaged scans of a particular ro-vibration line of both H_2O and H_2O_2 will be taken and stored on the micro-computer system. Also, high concentration hydrogen peroxide or pure water will be put in the 100% absorption cell, and their spectra will be recorded to be used in the final analysis. All cells will be pumped out until no absorption is present and the 100% transmission spectrum will be recorded to be used in the final analysis. The data files will then be processed in a computer program which will fit the H_2O_2 line to the Voigt line profile fitting program by using the calculated H_2O_2 concentration. Using these accurate line strengths, unknown H_2O_2 concentrations can be measured independently of any other calibration techniques.

26. Development and Evaluation of a New Preparation Technique for Producing High Accuracy Carbon Dioxide in Air Gravimetric Standards

R.C. Myers and G.A. Sleater

The atmospheric CO_2 measurement community has emphasized the need to achieve an absolute uncertainty of CO_2 in air standards of less than 0.4 ppm at the 95 percent confidence level. A new blending procedure for preparing high accuracy gravimetric primary standards has been developed in an attempt to evaluate the feasibility of further reducing the total uncertainty levels of SRMs, currently at 0.8 ppm.

The two errors that contribute to the uncertainty associated with the preparation of gravimetric primary standards are random errors and systematic errors or biases. These can be assessed to a high degree of precision through the use of "state-of-the-art" NDIR instrumentation. The reproducibility of measurements or precision of NDIR analyzers are numerically smaller than the total random error associated with preparing a set of primary calibration standards. Thus, the total random error of an internal set or sets of primary standards may be quantified by the deviation of predicted curve fit concentrations relative to the concentrations of the standards assigned by gravimetry. In addition, small systematic errors can be evaluated by the intercomparison of one set of primary standards to another.

One principal error which contributes to the total error in preparing gravimetric standards is the weighing of the minor component, CO_2. Previously, the reproducibility of the weighing measurements of the CO_2 has limited the uncertainty of primary standards to approximately ±0.3 ppm by mole at the 95 percent confidence level. These primary standards were prepared using a single-step dilution method by weighing approximately 0.2 g of CO_2 in a small cylinder on a semi-micro analytical balance.

A two-step dilution method was developed which allows a lower imprecision of CO_2 weighing measurements. In this method, a stainless steel cylinder having an approximate internal volume of 0.15L and weight of 600 g was filled with approximately 6 g of pre-analyzed CO_2. The cylinder was then weighed on a 0 to 1000 g analytical balance having a sensitivity of 100 micrograms against a similar cylinder which served as a tare. A mixture of approximately 1.5% CO_2 was blended from this.

This process was then repeated using the 1.5% mixture in place of the CO_2 reagent to produce several primary standards ranging from 300-400 ppm by mole in concentration. Several ppm-levels of CO_2 in air primary standards have been prepared from four 1.5% mixtures which were prepared at various periods of time over a nine-month period. Three different cylinders of reagent air were used in preparing the set of standards.

The set of primary standards was evaluated for internal consistency and also intercompared with the primary standards prepared using the single-step method. Predicted concentrations for each standard were confirmed directly from their NDIR voltages using a quadratic regression over the range of the standards. An average of the predicted concentrations from two NDIR analyses was calculated and compared to the gravimetric concentration of each standard. The estimated coefficient of variance was calculated at the 95 percent confidence level to be less than ± 0.2 ppm for the two-step dilution standards. Concentrations were predicted for the single-step dilution standards from the two-step dilution standards and the difference or systematic error was calculated to be 0.07 ppm. The two sets of primary standards are statistically indistinguishable since their uncertainties overlap.

27. Measurements of Sulfur-Containing Gases (OCS and CS2) in Ambient Air

R.L. Sams

Tunable diode laser absorption spectrometry (TDLAS) is probably one of the most versatile methods in use today for measuring trace atmospheric gases. This is especially true for the detection of the two sulfur-containing gases OCS and CS_2 which are well behaved and present no problem in detection and measurement.

The mixing ratio of OCS in ambient air has been previously reported to be about 400-500 parts per trillion by volume pptv; therefore, to adequately measure OCS in room air in real time, a very sensitive method has to be used. Previous measurements have been made by using preconcentration and then gas chromatography for the actual measurements. This is a slow (gathering samples) and uncertain (preconcentration factor) method at best. TDLAS is a continuous, rapid (3 s time constant or less) and accurate method well suited for measuring low concentrations of OCS encountered in the atmosphere. The strongest band for monitoring OCS is ν_1 at about 2060 cm^{-1}. An appropriate line was selected, P(21), and investigated under second derivative line-locked mode. The TDLAS was calibrated with an OCS permeation tube (20 ng/min) swept with 1 L/min zero air (5.7 ppbv). If only a line-locked second derivative mode was used, the measurement was subject to slow (minutes) background intensity fluctuations. This problem was overcome by adding a small second modulation at about 100 kHz. This additional modulation reduced the background fluctuation about two orders of magnitude to a more tenable size. Ambient air measured in this way was found to contain about 640±33 ppt of OCS, somewhat higher than previously measured.

Carbon disulfide is expected to have a much lower mixing ratio than OCS in ambient air about 40 pptv. The measurement of CS_2 was accomplished using a second derivative sweep-averaging technique. In this technique, the diode is modulated at about 11 kHz and also swept at 140 Hz. The detector signal is processed through a high speed lock-in amplifier (time constant less than 30 μs) and observed in the 2f mode. The output of the lock-in amplifier is averaged with a signal averager and saved for additional data reduction. It was found that a second modulation was helpful in reducing fringing effects with this technique. The addition modulation was supplied at 100 kHz with only a small amplitude required. Initial measurements on the ν_3 band of CS_2 leads to an ambient concentration of about 40±15 pptv. This large uncertainty is primarily due to excessive fringing. The detector noise is a factor of 10 to 100 less (1.5-.15 pptv). Additional work must be done on CS_2 to calibrate the measurements (CS_2 permeation tubes) and reduce the fringing noise to the detector noise limit.

C. Outputs and Interactions
(Gas and Particulate Science Division

1. Publications

Bright, D.S. and Steel, E.B., "Automated Analysis of Regular Spot Patterns in Electron Diffraction Images," Journal of Microscopy, June 1988, (in press).

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Currie, L.A., "Detection in Analytical Chemistry," Statistical Engineering Seminar, NBS, Gaithersburg, MD, November 10, 1987.

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Currie, L.A., "Detection in Radiobioassay: Concepts and Nomenclature," Environmental and Safety Division, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, Oak Ridge, TN, August 5, 1988.

Dorko, W.D., "Preparation and Verification of Gas Standards at Low Concentration Levels," Invited Continuing Education Seminar Series, Union Carbide Technical Center, Charlestown, WV, November 1987.

Dorko, W.D., "Gas Standards: NBS and the Specialty Gas Industry," Annual Quality Assurance Meeting of the Specialty Gas Division of MG Industries, December 1987. Invited

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Fletcher, R.A., "Microprobe Techniques with Emphasis on Laser Microprobe and Raman Microprobe" Department of Chemical and Nuclear Engineering, University of Maryland, College Park, MD, November 5, 1987.

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Steel, E.B., "SEM Imaging and Analysis of Submicrometer Particles in Air and Water Samples," Microbeam Analysis Society, Milwaukee, WI, August 1988.

Turner, S., "Use of High-Resolution TEM and Electron Diffraction to Study Fine-Grained Materials," American Crystallographic Association, Philadelphia, PA, May 1988.

Turner, S., "The Application of Quality Assurance to TEM Asbestos Analysis," ASTM Asbestos, Measurement Research and Laboratory Accreditation Conference, Johnson, VT, July 14, 1988.

Velapoldi, R.A., "The Determination of the Geologic Maturation Process Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy", Pittsburgh Conference, Poster Session, New Orleans, LA, February 1988.

Velapoldi, R.A., "Quality Assurance in Chemical Measurements," Quality Seminar Expo 88, Metrology Session, American Society for Quality Control, Oklahoma City, OK, March 2-3, 1988.

Velapoldi, R.A., "The Center for Analytical Chemistry and QA from Several Perspectives", IBM Analytical Laboratory Managers Annual Meeting, Mannassas, VA, April 1988.

Verkouteren, J.R., "PC-Access to Ceramic Phase Diagrams," ASTM Committee E-49, 1st International Symposium on Computerization and Networking of Materials Property Databases, November 1987.

Verkouteren, M.R., "Development of Isotope Dilution Mass Spectrometry for the Absolute Determination of Carbon Dioxide Abundance in Air," CAC Colloquium Series, June 13, 1988.

Zielinski, W.L., Jr., Hughes, E.E., Dorko, W.D., Rhoderick, G.C., and Myer, R.C., "Accuracy in Gaseous Standard Reference Materials," International Symposium on Trace Analysis in Environmental Samples and Standard Reference Materials, Honolulu, Hawaii, January 1988. Invited paper

Zielinski, W.L., Jr. and Rhoderick, G.C., "Cryogenic Preconcentration and GC-MS Analysis of Multicomponent Gas Standards of Volatile Toxic Organic Compounds at the Low ppb Level," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, February 1988.

Zielinski, W.L., Jr. and Rhoderick, G.C., "Assessment of Stability in Multicomponent Standards of Volatile Toxic Organic Compounds in the ppb Range," Symposium on Emissions from Combustion Processes: Origin, Measurement, Control: Sampling/Analytical Methodologies, 3rd Chemical Congress of North America, Toronto, Canada, June 1988. Invited paper

3. Committee Assignments

Rance A. Velapoldi
Interagency Toxic Substances Data Committee
ASTM E-07 on Nondestructive Testing
ASTM E-11 on Statistical Methods
ASTM E-13 on Molecular Spectroscopy
ASTM E-13.06 on Molecular Luminescence
ASTM E-13.06.01 on Presentation of Corrected Fluorescence Spectra
ASTM E-13.06.02 on Recommended Practices on Molecular Fluorescence Spectroscopy
Council for Optical Radiation Measurements (CORM)
Liaison (550), Council for Chemical Research (CCR)
Interagency Collaborative Group on Environmental Carcinogenesis

Arnold M. Bass
ASTM D-22 Sampling and Analysis of Atmospheres
ASTM D-22.01 Quality Assurance
ASTM D-22.03 Sampling and Analysis of Ambient Atmospheres
Ozone Science Guidance Committee, NESDZS

David S. Bright
ASTM E-29 Particle Size Measurement
ASTM E-29.04 Liquid Particle Measurement

Lloyd A. Currie
Radiocarbon Dating Quality Assurance Group
IUPAC Working Group on Chemometrics
CAC, Quality Assurance Task Force

Titular Member, IUPAC Commission on Analytical Nomenclature
Chairman, Consultant's Group, International Atomic Energy Agency, on Limit of Dete
University of Maryland Thesis Committee (A.E. Sheffield)
Editorial Board, Journal of Chemometrics
Organizing Committee, Mathematics in Chemistry Conference
Advisory Panel, Southern Methodist Univ. Geochronology Lab.
Advisory Group, Radiation Monitoring Quality Assurance and Quality Control Program, Martin Marietta Energy Systems ORNL

William D. Dorko
ASTM D-22 Sampling and Analysis of Atmospheres
Secretary, ASTM D-22.03 Sampling and Analysis of Ambient Atmospheres
NASA's Science Team for the Global Tropospheric Experiment Cite-3 Mission

Edgar S. Etz
ASTM E-13 Molecular Spectroscopy
ASTM E-13.08 Raman Spectroscopy

Robert L. Myklebust
ASTM E-2 Emission Spectroscopy
ASTM E-2.04 Standard Reference Materials

Dale E. Newbury
ASTM E-42 Surface Analysis
Journal of Microscopy, Editorial Review Board
Scanning, Editorial Review Board
J. Trace and Microprobe Techniques, Editorial Review Board
Journal of Electron Microscopy Techniques, Editorial Review Board

Peter A. Pella
ASTM E-22 Emission Spectroscopy
ASTM E-22.06 Statistics, Calibration and Standardization

Gerald A. Sleater
ASTM D-22 Sampling and Analysis of Atmospheres
ASTM D-22 Source Sampling

Walter L. Zielinski, Jr.
Interagency Committee on CO_2 and Climate
Interagency Committee for Stratospheric Ozone Protection
Interagency Committee for Indoor Air Quality
ASTM D-22 Sampling and Analysis of Atmospheres
Journal of Analytical Toxicology, Editorial Review Board
Editor, Critical Reviews in Analytical Chemistry

4. Other

a. Seminars

September 21, 1988

Dr. David Lowe, NCAR & DSIR, New Zealand, "Application of Accelerator Mass Spectrometry in Atmospheric Chemistry." (Division Sponsor: L. Currie)

July 7, 1988

B. Davis, South Dakota School of Mines & Technology, "A New XRD Method for Quantitative Analysis of Bulk Asbestos." (Division Sponsor: D. Johansen)

b. Conferences Sponsored

July 10-15, 1988

Harry L. Rook and Eric B. Steel, Johnson Conference.

July 19, 1988

P.A. Pella, Problems in the XRFS Analysis of Major and Trace Elements in Whole Coal.

December 15, 1987

W.L. Zielinski and W.D. Dorko, Workshop on Toxic Organic Gas Mixtures and the CRM Program.

August 1988

Dale E. Newbury, Workshop on Quantitative Electron Probe Microanalysis.

c. SRM Certification

Microanalysis

SRM 2063, Microanalysis Thin Film Mg-Si-Ca-Fe

X-Ray

SRM 600, Australian Bauxite
SRM 2704, Buffalo River Sediment
SRM 1219, Stainless Steel
SRM 1250 and 868, High Temperature Alloys
SRM 1276a, Cu-Ni Alloy
SRMs 1884 & 1889, Cements
SRM 1129, Electronic Flowsolder Powder
SRM 1623b & 1624b, Sulfur in Fuel Oil
SRM 1834, Simulated Fused Clay Materials
SRM 489, Ferrite in Austenite
SRM 1296, Stainless Steel
SRM 1568a, Rice Flour
SRM 1567a, Wheat Flour
SRM 1566a, Oyster Tissue
SRM 1548, Total Diet
SRM 1515, Apple Leaves
SRM 1547, Peach Leaves

Gas Metrology

- SRM 1625 10 cm SO_2 Permeation Tubes
- SRM 1626, 5 cm SO_2 Permeation Tubes
- SRM 1627, 2 cm SO_2 Permeation Tubes
- SRM 1629, NO_2 Permeation Tubes
- SRM 1693, 50 ppm SO_2 in Nitrogen
- SRM 1694, 100 ppm, SO_2 in Nitrogen
- SRM 1674, 7% CO_2 in Nitrogen
- SRM 1675, 14% CO_2 in Nitrogen
- SRM 1700, 10% CO_2 in Nitrogen
- SRM 1701, 5% CO_2 and 12% O_2 in Nitrogen
- SRM 1702, 5% CO_2 and 20% O_2 in Nitrogen
- SRM 1703, 10% CO_2 and 7% O_2 in Nitrogen
- SRM 1685, 250 ppm NO in Nitrogen
- SRM 1686, 500 ppm NO in Nitrogen
- SRM 1687, 1000 ppm NO in Nitrogen
- SRM 2725. 600 ppm C_3H_8 and 1.6% CO in Nitrogen
- SRM 2726, 3000 ppm C_3H_8 and 8% CO in Nitrogen
- SRM 2727, 600 ppm C_3H_2, 1.6% CO and 11% CO_2 in Nitrogen
- SRM 2728, 3000 ppm C_3H_8, 8% CO and 14% CO_2 in Nitrogen
- SRM 1681, 1000 ppm CO in Nitrogen
- SRM 2640, 4% CO in Nitrogen
- SRM 2641, 2% CO in Nitrogen
- SRM 1665, 3 ppm C_3H_8 in Air
- SRM 1666, 10 ppm C_3H_8 in Air
- SRM 1667, 50 ppm C_3H_8 in Air
- SRM 2730, 5 ppm H_2S in Nitrogen
- SRM 2731, 20 ppm H_2S in Nitrogen

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This report summarizes the technical activities of the Center for Analytical Chemistry at the National Institute of Standards and Technology. It emphasizes activities over the Fiscal Year 1988 in the Inorganic Analytical Research Division, the Organic Analytical Research Division, and the Gas and Particulate Science Division. In addition, it describes certain special activities in the Center including quality assurance and voluntary standardization coordination.

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Analytical chemistry; analytical services; gas and particulate science; inorganic analytical chemistry; organic analytical chemistry; quality assurance.

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