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Technical Activities 1986

Center for Analytical Chemistry

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U.S. DEPARTMENT OF COMMERCE
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R. A. Durst
H. S. Hertz
J. K. Taylor
R. A. Velapoldi

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Analytical Chemistry
Gaithersburg, MD 20899

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary
National Bureau of Standards, Ernest Ambler, Director

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I. Center for Analytical Chemistry

Harry S. Hertz, Director
Rance A. Velapoldi, Deputy Director
Richard A. Durst, Acting Deputy Director

A. Center Overview

The Center for Analytical Chemistry 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. Moreover, analytical measurements are increasingly used as the basis for industrial, regulatory, 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 breadth of 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 standard 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 - body fluids, plant and animal tissues, foods, hazardous chemical wastes, and high-technology materials. 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 references materials. As it is not reasonable to contemplate the development of SRMs to deal with every measurement problem, the Center's program must be multifaceted, 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.

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.

We are devoting considerable attention in the Center to better definition of our user communities and the various mechanisms for interacting with these communities. During the past year members of the CAC staff participated in 235 professional, technical, and standards committees. More than 150 tours of CAC laboratories took place. We co-sponsored/hosted several conferences, including a major conference in the area of biotechnology - the annual meeting of the Electrophoresis Society of the Americas. We have continued the process of visiting key members of our industrial constituency to obtain direct input to our planning process and to identify chemical measurement needs for the next few years and for the future. The number of guest scientists performing research in our laboratories increased by 50% during the past year to 80 guest scientists. We encourage this mode of interaction and invite researchers to work with us in areas where unique expertise or instrumentation exists at NBS. In some instances, this research at NBS may include work of a proprietary nature.

In September 1987, we will be sponsoring a symposium on Accuracy in Trace Analysis -- Accomplishments, Goals, Challenges. We look forward to this symposium with excitement, and welcome this opportunity to bring together the chemical measurement community to discuss the problems they are facing and the solutions which tomorrow's measurement technology must bring.

Directly related to our interactions with user communities is our major planning effort in chemical measurement services. As part of this activity, we have been seeking advice from constituents on the measurement science, measurement technology, and technology transfer needs which the Center must prepare for today, to deliver relevant services in the 1990's. We are in the process of conducting a broad-scale chemical measurement impact study. We invite input on topics to be included and on mechanisms for demonstrating the value added to industrial products through measurement. A major factor in our planning is the realization that in an era of increased reliance on voluntary standards it is vital, in our opinion, to assure the integrity of the measurement system through traceability to nationally accepted measurement standards. In this era, a scientifically accurate measurement base is the best support mechanism for both the industrial and regulatory sectors of the communities we serve.

The program of the Center strives 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 major recent activities and technical directions of the Divisions and groups are summarized. Much of the work in progress is omitted but will be included in subsequent Annual Reports.

B. Outputs and Interactions
(Center for Analytical Chemistry)

1. Publications

Durst, R. A., Chemically Modified Electrode Sensors, Ion-Selective Electrodes, Vol. 4, E. Pungor and I. Buzas, Eds., Akademiai Kiado, Budapest, 115-128 (1985).

Durst, R. A., Hertz, H. S., and Taylor, J. K., Technical Activities 1985 - Center for Analytical Chemistry, NBSIR 85-3272, 189 pages (Nov. 1985).

Durst, R. A., Clinical Electrode Potentiometry: Sources of Error, Reference Methods and Materials, Direct Piotentiometric Measurements in Blood, W. Koch, Ed., NCCLS Publication, 143-157 (1985).

Durst, R. A., Blubaugh, E. A., Bushong, W. C., and Shupack, S. I., Thermal Crosslinking Procedure for Preparing Solvent-Stable Polymer-Film Electrodes, Anal. Lett., in press.

Durst, R. A., and Blubaugh, E. A., Chemically Modified Electrode Sensors, Fundamentals and Applications of Chemical Sensors, D. Schuetzle and R. Hammerle, Eds., ACS Symposium Series #309, Washington, DC, 245-255 (1986).

Durst, R. A., Chemically Modified Electrode Sensors, Proceedings of the International Symposium on Ion-Selective Electrodes, Zhang, Z.-R., Ed., Shanghai, P. R. C., in press.

Durst, R. A. and Yap. W. T., Effects of Resistance and Capacitance on the Chronoamperometry of Polymer-Coated Electrodes as Modeled by a Finite Element Digital Simulation, J. Electroanal. Chem., in press.

Hertz, H. S., "Accuracy in Clinical Chemistry," Archives of Pathology and Laboratory Medicine, 1985, 109, 1066-1067.

Hertz, H. S., "An Overview of a National Reference System," A Reference System for Clinical Enzymology: Proceedings of the Workshop, Bowers, G. N., Edwards, G. C., Rand, R. N., Eds., NCCLS, 1-10 (1986).

Taylor, J. K., Impact of Instrumentation in Analytical Chemistry, in The History and Preservation of Chemical Instrumentation, J. T. Stock and M. V. Orna, Eds., D. Reidel Publishing Co. (1986) pp. 1-10.

Taylor, J. K., On Validation of Analytical Data, Marine Chem. 18, 115-9 (1986).

Taylor, J. K., Role of Collaborative and Cooperative Studies in Evaluation of Analytical Methods, J. Ass. Off. Anal. Chem. 69, 398-400 (1986).

Taylor, J. K. and Kratochvil, B., Sampling, in Metals Handbook, 9th Edition, Vol. 10, American Soc. for Metals, Metals Park, OH (1986) pp. 12-18.

Taylor, J. K., A Collection of Abstracts of Selected Publications Related to Quality Assurance of Chemical Measurements, NBSIR 86-3352, April 1986.

Taylor, J. K., Ed., Summary Report of NOAA-NBS Quality Assurance Workshop, NBSIR 1986.

Velapoldi, R. A., Liquid Standards in Fluorescence Spectrometry, Conference Proceedings, "Advances in Standards and Methodology in Spectrophotometry," Elsevier Publishing Co., The Netherlands, Accepted for Publication.

Velapoldi, R. A., Christy, A. A., Karstang, T., Kvalheim, O. M., Sletten, E., and Telnaes, Multivariate Calibration of Diffuse Reflectance Infrared Spectra of Coals as an Alternative to Rank Determination by Vitrinite Reflectance, Chemometrics and Intelligent Laboratory Systems, Accepted for Publication.

Welch, M. J., Cohen, A., Hertz, H. S., Ng, K. J., Schaffer, R., Van Der Lijn, P., and White V, E., Determination of Serum Creatinine by Isotope Dilution Mass Spectrometry as a Candidate Definitive Method, Analytical Chemistry, 1986, 58, 1681-1885.

2. Talks

Christy, A. A. and Velapoldi, R.A., "Diffuse Reflectance Spectroscopy" and "Coal Maturity by Diffuse Reflectance FT-IR," Chemistry Dept., University of Bergen, Bergen, Norway, March 1986. Invited

Christy, A. A. and Velapoldi, R. A., "Multivariate Calibration of Diffuse Reflectance FT-IR Spectra of Coals as an Alternative to Rank Determination by Vitrinite Reflectance, Conference on Chemometrics for Geologists, Ulvik, Norway, April 1986.

Durst, R. A., "Chemically Modified Electrode Sensors," Chemistry Department Seminar, Occidental College, Los Angeles, CA, January 17, 1986. Invited

Durst, R. A., "Electrochemistry," NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, April 16, 1986. Invited

Hertz, H. S., "Analytical Chemistry: State-of-the-Practice, State-of-the-Art, and the Importance of Each," Baton Rouge Analytical Instrument Discussion Group (BRAIDG), Baton Rouge, LA, October 2, 1985. Invited

Hertz, H. S., "NBS Chemical Measurement Services/Standard Reference Materials", Eli Lilly and Company, Indianapolis, IN, October 3, 1985. Invited

Hertz, H. S., "An Overview of a National Reference System," National Committee for Clinical Laboratory Standards and the National Reference System for the Clinical Laboratory, Workshop on a National Reference System for Clinical Enzymology, Arlington, VA, October 16, 1985. Invited

Hertz, H. S., "Opportunities in Chemistry at NBS," National Academy of Sciences, Washington, DC, October 22, 1985. Invited

Hertz, H. S., "The What, Why, and How of Future Chemical Measurements," CENTCOM Breakfast, 37th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 11, 1986. Invited

Hertz, H. S., "Implementing a Quality Assurance Program," 37th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 13, 1986. Invited

Hertz, H. S., "Laboratory Standards: 1) NBS Standard Reference Materials and QA Program, 2) Overview of the National Committee for Clinical Laboratory Standards Program," Association of State and Territorial Public Health Laboratory Directors, Charleston, S. Carolina, April 8, 1986. Invited

Hertz, H. S., "Current Research in Analytical Chemistry at NBS," The Procter and Gamble Company, Cincinnati, Ohio, July 24, 1986. Invited

Hertz, H. S., "The Clinical Laboratory Voluntary Standards Process in the U.S.," European Committee for Clinical Laboratory Standards Annual General Meeting, Cophenhagen, Denmark, August 12, 1986. Invited

Hertz, H. S., "Isotope Dilution Mass Spectrometry, An Accuracy Tie Point for the Clinical Chemistry Measurement System," Sixth International Symposium on Mass Spectrometry in the Life Sciences, State University of Ghent, Belgium, September 2, 1986. Invited

Taylor, J. K., "Quality Assurance of Chemical Measurements," LANL-NBS, Los Alamos, NM, October 2-3, 1985. Invited

Taylor, J. K., "Long-term Goals for Quality Assurance," NBS-NOAA Workshop, National Bureau of Standards, December 6, 1985. Invited

Taylor, J. K., "The Critical Relation of the Sample to Environmental Decisions," European Community Sampling Conference, Bilthoven, The Netherlands, January 21, 1986. Invited

Taylor, J. K., "The Role of Reference Materials in Environmental Analysis," European Community Sampling Conference, Bilthoven, The Netherlands, January 22, 1986. Invited

Taylor, J. K., "Statistics for Chemists," Pittsburgh Conference, Atlantic City, NJ, March 14, 1986. Invited

Taylor, J. K., "Quality Assurance of Chemical Measurements," Pittsburgh Conference, Atlantic City, NJ, March 14, 1986. Invited

Taylor, J. K., "Relation of Data Quality to Detection," ACS Meeting, New York, NY, April 16, 1986. Invited

Taylor, J. K., "ACS Principles for Environmental Analysis, Recommendations for Reporting Low-Level Data," ACS Meeting, New York, NY, April 16, 1986. Invited

Taylor, J. K., "Planning for Quality Data - IX Conference on Chemistry of the Mediterranean Sea," Primosten, Yugoslavia, May 7, 1986. Invited

Taylor, J. K., "Principles of Quality Assurance," Quebec Association for Advancement of Science, Montreal, Canada, May 12, 1986. Invited

Taylor, J. K., "Why Data Quality is so Important," Virginia Military Institute, Lexington, VA, July 19, 1986. Invited

Velapoldi, R. A., "Spectroscopy and Geology," Geology Division, Norsk Hydro, Bergen, Norway, January 1986.

Velapoldi, R. A., "Diffuse Reflectance FT-IR," Instrumentation Group, Norsk Hydro, Bergen, Norway, February 1986.

Velapoldi, R. A., "Total Internal Reflection FT-IR of Drilling Fluids," Well Technology Division, Norsk Hydro, Bergen, Norway, July 1986.

Velapoldi, R. A., Liquid Standards in Fluorescence Spectrometry, Conference on "Advances in Standards and Methodology in Spectrophotometry," Held at Keble College, Oxford, September 16, 1986. Invited

3. Committee Assignments

Harry S. Hertz
- President, National Committee for Clinical Laboratory Standards
- Chairman, Education Committee, American Society for Mass Spectrometry
- Member, ASTM, Committee D19 on Water
  - Committee E48 on Biotechnology
- Member, Analytical Laboratory Managers' Association
- Member, Department of Energy, Health and Environmental Research Advisory Committee
- *Analytical Chemistry* Editorial Advisory Board
- Technical Advisor, OIML, SP26, Subcommittee SR5 on Reference Materials for Calibration of Instruments Meant for Checking Substances During Medico-Biological and Research Analyses

Richard A. Durst
- Member, ASTM, Committee D19 on Water
- Member, ASTM, Committee E-48 on Biotechnology
- Member, Board of Advisory Editors, Ion-Selective Electrode Reviews
- Member, IUPAC, Committee V on Analytical Chemistry
  - Subcommittee 5 on Electroanalytical Chemistry
- Member, NCCLS, Subcommittee on Electroanalytical Methods
  - Subcommittee on pH and Blood Gases
- Member, NBS, Research Advisory Committee
- Member, DoC, Biotechnology Working Committee

John K. Taylor
- Member, 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
- Chairman, ASTM D19.01, International Standards
  - ASTM D22, Sampling and Analysis of Atmospheres
- Member, 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
NBS Representative - Interagency Advisory Committee on Water Data

4. Courses Taught

Harry S. Hertz

"Interpretation of Mass Spectra," ASMS Annual Conference on Mass Spectrometry and Allied Topics, Cincinnati, OH, June 7-8, 1986.

John K. Taylor

"Quality Assurance of Chemical Measurements," Shell Development, ACS Short Course, Houston, TX, October 8-10, 1985.

"Quality Assurance of Chemical Measurements," Nuclear Regulatory Commission, National Bureau of Standards, Gaithersburg, MD, October 29-31, 1986.

"Quality Assurance of Chemical Measurements," EPA-Region II, National Bureau of Standards, Edison, NJ, November 13-14, 1985.

"Quality Assurance of Chemical Measurements," National Bureau of Standards, December 3-4, 1985.

"Quality Assurance of Chemical Measurements," Ratheon, ACS Short Course, Grande Isle, MI, December 10-11, 1985.

"Quality Assurance of Chemical Measurements," United Technologies, ACS Short Course, West Palm Beach, FL, February 5-6, 1986.

"Quality Assurance of Chemical Measurements," Atlantic City, NJ, ACS Short Course, March 8-9, 1986.

"Quality Assurance of Chemical Measurements," ALCOA, ACS Short Course, Pittsburgh, PA, April 20-21, 1986.

"Quality Assurance of Chemical Measurements," Alberta Environmental Center, ACS Short Course, June 18-19, 1986.

"Quality Assurance of Chemical Measurements," Tri-Cities University, ACS Short Course, Edmonton, Canada, June 25-26, 1986.

"Quality Assurance of Chemical Measurements," ACS Short Course, Anaheim, CA, September 6-7, 1986.

"Quality Assurance of Chemical Measurements," ACS Short Course, St. Louis, MO, September 26-27, 1986.

5. Sessions Chaired

Harry S. Hertz
"Quantitative Mass Spectrometry," Sixth International Symposium on Mass Spectrometry in the Life Sciences, Ghent, Belgium, September 2, 1986.

6. Center Colloquium Series

October 30, 1985	-	Dr. Louis Meites, Chairman Department of Chemistry, George Mason University, Fairfax, Virginia, "Thermometric Titrimetry Through the Ages."
November 13, 1985	-	Dr. Douglas Donahue, Department of Physics, University of Arizona, Tucson, Arizona, "Application of Accelerator Mass Spectrometry to Some Problems in Archeology and Geophysics."
April 9, 1986	-	Dr. Catherine E. Costello, Department of Chemistry Massachusetts Institute of Technology, Cambridge, Massachusetts, "Adventures with a New High-Field Four-Sector Mass Spectrometer."
May 14, 1986	-	Dr. George Morrison, Department of Chemistry, Cornell University, Ithaca, New York, "Ion Microscopy in Biology and Medicine."
May 15, 1986	-	Dr. Dennis Schuetzle, Chemical Analysis Research Department, Ford Motor Company, Dearborn, Michigan, "Recent Advances in ESCA and SIMS."
June 11, 1986	-	Dr. Jeannette Grasselli, Research and Development Division, Standard Oil Company (SOHIO), Cleveland, Ohio, "The Challenge and Opportunity for Analytical Chemistry in Industry."
September 10, 1986	-	Dr. Edmund R. Malinowski, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, "Introduction to Factor Analysis in Analytical Chemistry."

C. Voluntary Standardization and Quality Assurance

1. Voluntary Standardization

John K. Taylor

The Center continues to play an important role in standardization activities. Twenty-nine members of the staff hold 154 memberships on standards committees, including positions of leaderships on 10 of these, as follows:

ASTM C-26	Nuclear Fuel Cycle
ASTM D-19	Water
ASTM D-22	Sampling and Analysis of Atmospheres
ASTM E-02	Emission Spectroscopy
ASTM E-03	Chemical Analysis of Metals
ASTM E-07	Nondestructive Testing
ISO/TC146	Air Quality
ISO/TC147	Water Quality
IUPAC	Commission on Atomic Weights
NCCLS	National Committee for Clinical Laboratory Standards

Leadership was provided in organizing the 1986 Johnson Conference of ASTM Committee D22 on Sampling and Analysis of Atmospheres. The conference dealt with the currently important issues of asbestos measurement, indoor air monitoring, and the analysis of acid rain. Five center scientists made important contributions to this conference - a number of Center scientists also are cooperating with the USA Reporting Secretariat PS17/R52 of International Organization for Legal Metrology in developing performance standards for analytical instrumentation of pollution monitoring.

2. Quality Assurance

The Center's program to provide quality assurance education and assistance to other government agencies and to the public has been very active during the past year. A key feature of this is the Quality Assurance Seminar series initiated in 1983. These seminars are of two types: those held at NBS consist of 10 hours of lectures and 4 hours of small-group discussions (mini-workshops) in selected measurement areas; those presented away from NBS consist entirely of 16 hours of lectures given during a two-day period. Essentially the same material is presented in the lectures of both seminars, except that the content is enlarged in the case of the latter type. One seminar of the first type was presented at NBS with an attendance of 45 persons. A special seminar of the second type was presented at NBS to personnel of the Nuclear Regulatory Commission. A similar seminar was given at the Los Alamos National Laboratory and five seminars were presented with ACS sponsorship at two national meetings and at three industrial organizations.

Special cooperation has been provided to the Army's Edgewood operations. A comprehensive survey was made and advice provided on the Army Industrial Hygiene Agency's contract laboratory program. In addition I have served throughout this year as an advisory member of the quality assurance task-group of the Chemical Research, Development, and Engineering Corps.

In special cooperation with EPA, I am an advisory member of a special task group whose mission is to develop guidelines for admission and coding of data to STORET Computerized Water Quality Database.

NBS Special Publication 260-100, "Handbook for SRM Users," was published at the beginning of the year and its initial printing of 5000 copies is about exhausted. It has been slightly revised and reprinted. This handbook provides information on the role of SRMs for quality assessment of analytical data and gives guidance on how to use them effectively to evaluate measurement accuracy. The systematic measurement of SRMs, along with a laboratory's own control samples with all results interpreted by means of control charts, is proposed as the most effective way to accomplish this purpose.

The center has organized a quality assurance task group that is developing selected aspects of its QA program. During the year, the group has developed a document setting forth policy and guidance for laboratory record keeping as well as a form for use in defining the work to be done in service analysis or for SRM certification measurements. A document providing guidance for the more uniform statistical treatment of measurement data also has been prepared.

D. Service Analysis

R. W. Burke and M. V. Smith

The performance of service analyses continues to be an important function of the Center for Analytical Chemistry (CAC). Within the scope of this activity, the technical staff gives advice, performs accurate chemical analyses, and provides state-of-the-art calibrations on a wide range of research and standard materials. This service is available, on request, to NBS staff and to all Federal, state, and local government groups. It is also available for use by the private sector in those special instances for which CAC possesses a unique measurement capability. Within the latter category, the two most frequent types of requests are for the verification of spectrophotometric transmittance SRMs and for the recalibration of SRM gas mixtures.

In the performance of the service analysis function, every member of the CAC staff is dedicated to providing timely, cost effective, and informative analyses. The turnaround time for the more straight-forward analyses ranges typically from several days to about two weeks. All work is performed on a cost reimbursable basis. Within NBS, funds are obligated on an interdivision work order and designated cost centers are cross-charged. All outside work is performed on a purchase order.

During the first 11 months of FY86, CAC staff provided analyses or recalibrations for some 110 requests at a cost of $208,020. These requests and their associated funding were divided among the three categories of customers as follows: NBS - 25 jobs ($88,730); other government agencies - 21 jobs ($56,050); and private industry - 65 jobs ($63,240).

Historically, other government agencies have spent the most dollars on service analyses. This year, expenditures in this category was markedly lower than in previous years ($75K decrease from FY85). This decrease is likely due to cutbacks resulting from Gramm-Rudman legislation. The number of requests and level of funding from NBS and private industry were about on a par with past years.

II. Inorganic Analytical Research Division

James R. DeVoe, Chief
Barry I. Diamondstone, 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 new principles of 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.

The implementation of a new data base, containing analytical values obtained for SRM certification, has resulted in increased attention being paid to the intercomparison of results among analytical methods. This capability to rapidly identify discrepancies has led to an increased effort in the Division to evaluate sources of bias for various analytical procedures. Numerous activities are in progress that are aimed at producing new and more effective chemical separations. There are three projects underway that involve the use of liquid chromatography (LC), each using a different approach (one involves the separation of alkali metals from the transition metals using robotics, one uses ion chromatography, and one uses high performance liquid chromatography (HPLC)). The major thrust of this work has been in the area of atomic spectroscopy since Division analysts are especially sensitive to the need to matrix match for improving accuracy in this area. However, it is expected that very high resolution LC will prove to be useful with many of the analytical techniques. Our fledgling effort in the use of robots has the potential for significant impact (as indicated in a following report). We are actively studying the meaning and use of the so-called expert systems which may be adapted to optimize chemical separations with respect to the analytical method as well as to the sample being analyzed. A decision has been made to reemphasize wet chemistry followed by gravimetry and/or spectrophotometry for the high accuracy measurement of certain macro and minor constituents such as silicon and phosphorus. In the future, it is possible that improvements to existing techniques, such as isotope dilution mass spectrometry (IDMS), can be used for such purposes, but in the meantime at least one man-year will be devoted to reestablishing classical techniques.

During the past year, funds have been made available to upgrade and refurbish a number of laboratories. One existing clean room on the third floor of the Chemistry building that was more than 15 years old was completely rebuilt using state-of-the-art clean room facilities. This effectively doubles the clean room space which has been very much needed. Division personnel, experienced in clean room design and use, were available to help design the new facility and to oversee the implementation of the refurbishing process. In addition, work has begun on the renovation of the radiochemical laboratories in the Reactor Building. This will allow the rest of the Division staff to utilize tracer techniques, with their inherent high sensitivity, to investigate problems such as losses of elemental constituents during chemical dissolution.

The Division has been fortunate to have a number of guest workers with us from The Peoples' Republic of China. They have been of inestimable assistance by helping to certify SRMs while, at the same time, they have had the opportunity to learn some of the new methods that have been developed at NBS. Without exception, these guest scientists have been eager to learn and have proven to be very capable.

There have been significant advances in the developmental research area this past year, and some of these are detailed in the various reports that follow. Several have not been included but are of equal importance. For example:

> Ion chromatographic methods have been developed and applied to the determination of alkali and alkaline earth metals at trace and ultratrace levels.
>
> The development of a high accuracy analytical procedure for CO_2 by isotope dilution mass spectrometry has progressed well during the last year.
>
> Extensive improvements have been made in the type of standards that are currently available for the calibration of spectrophotometers.
>
> Significant progress has been made in determining the extent to which resonance ionization mass spectrometry can be used to measure high isotopic abundance ratios.
>
> The determination of arsenic in human livers by instrumental neutron activation analysis, the institution of specimen banking for NOAA, and participation in a number of "round-robin" studies such as the analysis of selenium and zinc for NIH, as well as the analysis of a variety of steels for C and S for the International Organization for Standardization (ISO), have all been part of the research activities carried out in the Division during the past year.

The concept of Technical Champions, which was initiated last year, has become a major part of Division efforts in the analysis of SRMs. More than a dozen senior scientists have taken the responsibility of overseeing the technical aspects of forthcoming SRMs. The ultimate goal of this program is closer interaction between the members of the Division and the project managers of the Office of Standard Reference Materials.

Long-range planning is carried out while taking into account two main considerations which operate under a degree of counterpoise. Projects are planned on the principle that, in the long run, the results of R&D will produce an improvement in the accuracy of chemical analyses. This means that emphasis is placed upon techniques such as isotope dilution mass spectrometry that have the requisite high accuracy. This method and nuclear activation analysis are our most expensive techniques, but the resulting accuracy is worth the investment. If accuracy is taken as the ultimate consideration, then these two methods should be the mainstays in the certification of Standard Reference Materials. On the other hand, if fiscal constraints such as the need for the Office of Standard Reference Materials to reduce the cost of the certification of SRMs is considered, there is considerable interest in doing R&D on the accuracy of techniques that are less costly, and as a consequence, are widely used in industry. Such techniques are the optical, atomic, ion chromatographic, and electrochemical methods.

Taking all of the above considerations into account, our long range plans are as follows:

1. Perform developmental research in the area of IDMS by trying to automate various parts of the analysis without sacrificing accuracy, in order to reduce the cost of this technique. (Examples are the automation of chemical separations via HPLC, R&D on the ICP-MS, and the purchase of the new multi-source and detector mass spectrometer).

2. Perform R&D to improve the accuracy of the optical, ion chromatographic, and electrochemical techniques.

3. Institute greater use of technicians for the certification of SRMs by all techniques. Since there is always the danger of sacrificing accuracy by doing this, a much greater emphasis will be placed on quality assurance coupled with very close supervision by the senior staff.

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 isotopic 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.

Two new commercial mass spectrometers have been acquired by the Group in the past two years. Last year, an inductively coupled plasma mass spectrometer (ICP-MS) was installed and made operational. This instrument has been intensively studied this year for its ability to make high-sensitivity isotope dilution measurements directly from aqueous solutions. Very promising experiments have been completed which compare isotope ratio measurements of this instrument with thermal ionization. An NRC-NBS postdoctoral associate has joined the group this year and has begun experiments to interface the ICP-MS to a liquid chromatograph to do elemental speciation studies.

A second instrument, an automated multi-collector thermal ionization mass spectrometer, has been purchased, and installed this year. The purchase of this instrument represents a dramatic departure from tradition, since, historically, the Group has operated only NBS-built thermal ionization mass spectrometers. The multi-turret source and automated capabilities promise to increase sample throughput and the multi-collector can make high-precision measurement more routine. Further studies are required to demonstrate accuracy.

Progress continues to be made in the resonance ionization mass spectrometry (RIMS) program. The capabilities for osmium and rhenium isotopic measurement by RIMS have been extended to the sub-nanogram levels. The incorporation of a measurement system based upon signal averaging or pulse counting, using a transient-digitizer, has been evaluated and is now in operation. A high-resolution laser system has been built and is used with our second RIMS instrument. This system has recently been used to demonstrate isotopically-selective resonance ionization; the first isotopic shift measurements have been made for beryllium. In collaboration with researchers from the Centers for Radiation Research and Chemical Physics, instrumentation for laser desorption and ion sputtering studies is being developed and preliminary results have been obtained.

Research and development work on a microwave digestive system has continued. By use of probes that measure the pressure and temperature in closed vessels in a microwave oven, power absorption data can be collected during acid decomposition of samples. These data have then been used to generalize the technique for different heating conditions and samples. Through collaborative research with a number of analytical groups outside NBS, the usefulness of microwave dissolution has been demonstrated for many types of samples.

The use of robots for the automation of chemical separations is being investigated. Training a robot to do some of the more routine, yet vital functions of the Group's chemistry has been and will continue to be challenging.

Since accurate isotope ratio measurements have always been the Group's strength, we have been very active in this over the past year. Significant progress has been made on the chemical assay and isotopic analysis of nickel, such that the redetermination of the atomic weight of nickel should be completed next year. High sensitivity measurements of uranium have continued in support of a number of programs, including one using the reduction of background for a multi-national experiment involving proton decay. The Group has also made significant contributions to the certification of various Standard Reference Materials.

In the future, the general research program of the inorganic mass spectrometry group will be directed toward traditional goals of improving sensitivity, applicability, precision and accuracy of isotope ratio measurement. The program will encompass state-of-the-art instrumentation (ICP-MS, RIMS, HPLC) and emerging ideas and concerns in inorganic analysis (automation, inorganic chromatography, multicomponent analysis). The Group will continue to develop low blank methods of chemical separation and high sensitivity methods of ionization to certify elements at ultratrace levels in a variety of important materials (Se, Zn, V in serum; B, S in steel; Os, Re in rocks; U, Th in water). The Group will become more involved in new areas of isotope metrology, such as: the use of isotopic tracers in environmental and nutrition studies, the development of new atomization techniques for laser mass spectrometry, and the measurement of radioactivity by mass spectrometry. And finally, the Group will be actively pursuing the introduction of automation in the laboratory, both in mass spectrometry (evaluation of fully automated mass spectrometers) and in the chemistry (robotics), which promises to provide increased throughput and reproducibility for the more routine measurements.

Jack D. Fassett, Group Leader; I. Lynus Barnes, Ellyn S. Beary, William A. Bowman, III, Karen A. Brletic, Courtney A. Clements, Emile C. Deal, John W. Gramlich, Scott A. Hotes, Lois B. Jassie, W. Robert Kelly, Howard M. Kingston, George M. Lambert, John R. Moody, Paul J. Paulsen, Ronald W. Shideler, Heinz Zeininger, and Richard J. Walker.

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 methodology. Research and development activities include areas of atomic emission, absorption, and fluorescence spectroscopy, as well as resonance ionization mass spectroscopy, and the application of lasers to ionization processes, e.g., laser enhanced ionization in flames and photoionization processes in mass spectrometry (RIMS). 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).

The testing of SRMs for homogeneity and their subsequent certification continues to be a major activity of the Group. Over 110 elements were determined in a total of 30 SRMs using all of the established analytical techniques in the Group. In particular, the determination of 12 elements in Dolomitic Limestone will result in the renewal of this SRM with low uncertainty limits for most of the elements determined. The homogeneity assessment and acceptance testing of the new 1760 series low alloy steel SRMs using spark emission spectrometry marks the first step in a major effort to replace the depleted 1260 series. We have analyzed a number of materials for other government agencies. For example, participation in round-robin studies has continued in support of a National Cancer Institute study of Se and Zn in blood using atomic absorption spectrometry, and in ISO and ASTM studies of C, S, O, and H in steels using inert gas fusion techniques.

Research in laser enhanced ionization has been continued by one of the Group members (G.C. Turk) who is on sabbatical at ISPRA working with N.I. Omenetto. Laser probes in chemical flames, coupled with electrical detection have been used to study ionization efficiencies and spectroscopic lifetimes. This new approach allows the comparison of ion depletion rates due to recombination and fast chemical reaction processes in the flame.

Several group members have collaborated with the mass spectrometry group on the resonance ionization mass spectrometry (RIMS) project. Very narrow laser linewidths, combined with an opposed beam geometry resulted in excitation to the ion with Doppler-free linewidths being produced. Using this instrument, optical isotope shifts have been measured for a number of the atomic transitions in beryllium.

Research on separation techniques for improving the accuracy and precision of trace element determinations has continued in three major areas. The first involves the application of HPLC for the separation of major constituents from trace elements in complex matrices. The goal is to provide a means for atomic and molecular instrumental measurement techniques to determine trace elements without systematic errors due to the presence of the sample matrix elements. Initial efforts have focussed on the characterization of solvent and apparatus materials compatibility to minimize sample contamination. The second area is the use of ion chromatography for the separation of phosphorus from iron and copper matrices prior to determination by direct current plasma spectrometry. The quantitative separation of P from solutions of copper benchmark SRMs eliminated an unresolvable spectral interference from Cu in the DCP emission spectrum. The third area of research involves the use of HPLC coupled with AAS. The system developed last year to preconcentrate Cr^{+6} from aqueous mixtures of Cr^{+3} and Cr^{+6} has been modified to allow the separation and determination of both Cr^{+3} and Cr^{+6} in natural waters and sediment leachates. The group has contributed expertise in software and instrument-computer interfacing design to a project to apply robotics to automated sample preparation and chemical separation in collaboration with the mass spectrometry group.

Research in calibration statistics has led to a new method for estimating uncertainties for calibration curves. The specific application is for linear calibration curves over concentration ranges of several orders of magnitude. Non-constant variance (heteroscedasticity) is usually exhibited by measurements over such a wide range, and special techniques must be employed to account for the changing variance.

Material transport research has continued with the examination of accuracy in solid sampling of aluminum matrices. Progress in aerosol generation, transport and collection techniques has led to the development of a method for real-time analysis of ambient aerosols. Single element detection has been demonstrated using regenerative blower sampling coupled to atomic absorption spectroscopy (AAS). The entire system is portable and will be used to monitor Fe aerosols in air.

Optical absorbance filters continue to be important SRMs for spectrophotometric measurements in industry, as evidenced by the high demand for these SRMs. Research in this area has resulted in significant advances in the characterization of these filters. The precise measurement of substrate, coating thickness, and transmittance (T) uniformity is now automated and implemented on a routine basis. The calibrated range of transmittance has been extended from 10-30 %T to 1-50 %T. A new technique for producing solid fluorescence standards has been developed using sintered phosphorus compounds and powdered Teflon. Twelve sets of these new materials have been delivered to other laboratories for evaluation.

The Group has determined that wet chemical analysis techniques must be re-instituted and that expertise in this area be maintained to complement instrumental spectrometry. We also expect to use existing instrumental spectrometry to improve the accuracy of the classical techniques.

The Group has maintained its high level of cooperative research with NBS and other visiting scientists. R. Paule, National Measurement Laboratory, has collaborated with F.C. Ruegg on the analysis and graphical presentation of interlaboratory data from the National Cancer Institute. R. Christensen, Liquid Chromatography Group, Prof. A. Syty, Indiana University of Pennsylvania, and T.C. Rains have continued their studies on chromatographic separations coupled to AAS. R. Christensen has also consulted with R.W. Burke on metal chelate separations using HPLC. C. Spiegelman, Center for Applied Mathematics, Prof. R. Carroll, University of North Carolina, Chapel Hill, and R.L. Watters, Jr. have developed the heteroscedastic calibration method. N. Valette-Silver, University of Maryland, N. Boctor, Carnegie Institute of Washington, and R.L. Watters, Jr. have applied ICP spectrometry to the study of geothermal fluids and deposits. M.S. Epstein is working with K. Epler, University of Maryland on coupling ion chromatography to DCP spectrometry as part of Ms. Epler's doctoral research with Prof. T. O'Haver.

In the future, the Group plans to apply some of the emerging laser techniques to the accurate analysis of SRMs. The Laser Enhanced Ionization (LEI) technique has matured to the point that specific matrices can be analyzed for trace elements at sub ng/mL concentrations. As sources of systematic error in new matrices are defined, and the sensitivity and selectivity are improved, the capability of LEI as an accurate method will be evaluated for a number of new materials. We expect to develop fluorescence techniques using both laser and broad-band sources, and the hollow cathode discharge will be investigated as a source of atomic vapor for spectrometric analysis. Chromatography will play an increasingly important role both for chemical speciation and for pretreatment of complex samples to reduce systematic errors in instrumental spectrometric analysis. Matrix element separation schemes will also be investigated as a means of reducing errors in absorption or emission spectrometry. Since these schemes often involve the use of a variety of organic and inorganic solvents, new spectrometric calibration effects with AAS, ICP, DCP, and LEI will be characterized. We also expect that existing spectrometric techniques will be used to analyze intermediate fractions of classical separations for major element determinations. This will eliminate the need for multiple separations often required to make classical analysis techniques accurate.

Robert L. Watters, Jr., Group Leader; Robert W. Burke, Therese A. Butler, Barry I. Diamondstone, Katherine Epler, Michael S. Epstein, Robert C. Gauer, R. Eben Jenkins, Radu Mavrodineanu, John A. Norris, Theodore C. Rains, Fillmer C. Ruegg, Theresa A. Rush, Melody V. Smith, John C. Travis, Gregory C. Turk, Thomas W. Vetter, Jesse Wen, and Laura J. Wood.

3. Electroanalytical Research Group: Overview

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

The Group's interest in accurate measurements in acid rain has continued along three major lines: a) continued checking of SRM 2694, Simulated Rainwater, for long-term stability, b) studying the effects of radiation sterilization on long-term stability of rainwater standards and groundwater standards, c) working with ASTM to establish a standard method for the measurement of pH, anions, cations, conductivity, and acidity in rainwater. SRM 2694 has been reanalyzed one year after its initial production. Minor changes were noted in pH and sulfate; a significant change was observed in the nitrate concentration of Level 1. These changes resulted in a revision to the Certificate of Analysis. Rechecks of SRM 2694 are planned at six month intervals. It is hoped that the irradiation study started this year will remedy these instability problems.

A Research Associateship Project has been established in the Electroanalytical Research Group in conjunction with the National Committee for Clinical Laboratory Standards (NCCLS), and the Council of the National Reference System for the Clinical Laboratory. The purpose of this project is to develop reference methodology for measuring by direct potentiometry with ion selective electrodes, the activity of free ionized sodium, potassium, and calcium in blood. Definitive and reference methods, and certified reference materials for measurement of each element's total concentration are currently available. However, the increased use of ion selective electrodes requires that a reference method be developed to measure each element's activity.

Through financial sponsorship by industrial manufacturers of direct potentiometric analyzers, the NCCLS and the Council have hired a postdoctoral research associate, Dr. P. Chandrani Gunaratna, to work under the direct supervision of the senior staff in the Group. Initial efforts have concentrated on developing the necessary skills and experience in this new endeavor. A new cell design has been developed, which, along with an ammonium chloride filling solution, minimizes liquid junction potential biases in a serum matrix. Work is proceeding to use a sodium amalgam cell to improve the accuracy of the determination of the activity of sodium ion.

Research is continuing on the development of aqueous electrolytic standards. A Jones Bridge has been acquired and has been recalibrated by the Electricity Division at NBS. Other instrumentation necessary for the measurement of conductance has been improved and tested. The oil bath used for temperature control has been improved, with temperature stability to 0.001 °C at 25 °C. A new cell that will give an absolute measure of cell constant, has been designed and fabricated. Preliminary testing shows that this novel approach using a cell with variable, but accurately known cell length is feasible and theoretically accurate. Modifications to the cell are being made. Collaborations with Professor Robert L. Kay at Carnegie-Mellon and with Anna Tomek at the Office of Measures in Hungary have been established.

Research in electrolyte theory has been initiated, and consultations with noted experts (Harold Friedman, Walter Hamer, Vincent Bower, Robert Kay, and Arthur Covington) in the field have been held in an endeavor to improve the state of pH measurements and standards, which will ultimately lead to a single, unified pH scale. Dr. Rabindra Roy from Drury College, Springfield, Missouri has joined the Electroanalytical Research Group on an IPA assignment for the summer. His research project has been to develop, by using the Harned cell, an accurate data base which is necessary for the development of high ionic strength pH buffer standards that have applications in oceanography and clinical chemistry.

Research in voltammetry is progressing well: a new microprocessor-controlled voltammeter has been acquired which will permit determinations with lower detection limits and includes capabilities in ASV, cyclic, and differential pulse polarography. A project done in collaboration with the mass spectrometry group has resulted in the development of improved dissolution procedures incorporating microwave digestion. This required the development of voltammetric techniques to detect traces of undigested organics. Applications include bovine liver and monel. The use of indium as an internal standard in anodic stripping voltammetry has been developed and applied as a means of improving its accuracy and precision. The vibrating wire electrode has been used as a detector in the ion chromatographic determination of iodide with a ten-fold enhancement in sensitivity over the static electrode. Additional research is needed to fully develop the procedure.

Methods have been developed for the ion chromatographic determination of sodium, potassium, ammonium, calcium, and magnesium. Anion determinations have been improved with the implementation of a new micromembrane suppressor system; a similar system has been installed for the cations. Using concentrator columns, determinations of calcium at the parts per trillion level have been made. Attempts to use ion chromatography for the determination of fluoride in botanicals at natural levels proved impractical due to interferences. Instead, a method was developed using ion-selective electrodes after high-pressure oxygen bomb combustion. This method was used to determine the concentration of fluoride as a function of particle size in timothy grass, a candidate SRM. A joint research project with the Atomic and Molecular Spectroscopy Group, aided by a graduate student from the University of Maryland, which couples ion chromatography to direct current plasma spectrometry has been initiated. Separations of several metals have been achieved, and a procedure for eliminating the copper interference from phosphorous has been developed. Research is beginning on the implementation of replacement chromatography followed by atomic spectrometry.

As always, SRM certification and other service analyses have been an important part of the Electroanalytical Research Group's activities. Sulfur in various oils and fuels has been determined by ion chromatography. Combustion gases have been analyzed for chloride, bromide, and cyanide. The trace ionic impurities on filters have been measured. Potassium tetroxalate has been recertified as a pH buffer standard. Monel has been analyzed for lead and copper. Potassium dichromate and calcium carbonate have been assayed by controlled-current coulometry. A joint project with the Electrodeposition Group of the Metallurgy Division involving plating characteristics of various materials has continued for a second year.

The Electroanalytical Research Group continues to expand its resources and scope of research through active use of the guest worker program, and industrial, international, and academic collaborations. This year the group is composed of four research chemists, a guest worker from the People's Republic of China, two summer students, a research associate, and two visiting professors. The group maintains its involvement with ASTM and NCCLS through participation in meetings and task groups, and has been active in Task Group IV (Monitoring) of the National Acid Precipitation Assessment Program. 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. Investigations in aqueous conductance will continue; advancements in ion chromatography will be explored. Flow-injection analysis with electrochemical detection will be implemented for determinations of trace metals in complex matrices. Voltammetry will be used extensively as a valuable analytical research technique within the group. Speciation of metals by valence and by complexation will be a dominant research direction.

William F. Koch, Group Leader; George Marinenko, Yung Chi Wu, Kenneth W. Pratt, Melissa Knoerdel, Lisa A. Holland, Han Kai, P. Chandrani Gunaratna, Rabindra Roy, and Clarence H. Breedlove.

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, using 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 our involvement in the 7th International Conference on Modern Trends in Activation Analysis, by new measurements carried out at other research facilities, and by a major renovation of laboratory space in the Reactor Building. The MTAA-7 meeting, which was held in Copenhagen in June, commemorated the fiftieth anniversary of the discovery of activation analysis by Hevesy and Levi. NBS scientists were authors of ten of the papers presented at this conference. The opportunity was also provided for visits to the laboratories of several of our European colleagues.

In addition to our on-going use of the nearby reactors at the University of Maryland and the University of Virginia, primarily for fast and epithermal neutron activation analysis, Group members carried out measurements using the facilities at the new cold neutron source at Jülich and the intense guided thermal neutron beam at Grenoble. The Jülich work, which was reported at the MTAA-7, provided the first demonstration of the use of a cold neutron beam for prompt gamma activation analysis. At the ILL Grenoble reactor, which currently has the world's most intense thermal neutron beam, the neutron depth profiling facility was used to demonstrate the profiling of oxygen with the $^{17}O(n,\alpha)^{14}C$ reaction. This work has since been repeated on the NBS facility, but to be practical, the actual implementation of NDP for oxygen must await the very intense beams of the proposed NBS Cold Neutron Facility.

The Group's contribution to the certification of Standard Reference Materials is illustrated by the multielement measurements done on the following SRMs: Fly Ash, Flint Clay, Plastic Clay, Dolomitic Limestone, Rice Flour, and Wheat Flour. At major levels, the determination of silicon by fast neutron activation analysis has been demonstrated. Preliminary measurements of trace levels of lithium and boron in biological materials will be published using a thermal neutron irradiation followed by a helium gas mass spectrometric determination for quantification.

Research into biomedical problems has again been strong this year centered around the activities of the joint NBS/NOAA/EPA Environmental Specimen Bank. A new stable isotope technique for the measurement of total blood volume in humans has been reported based on the NAA determination of the Cr-51/Fe-59 ratio in samples spiked with Cr-50. The characterization of biological macromolecules by a combination of gel electrophoresis and neutron activation analysis is under development. A special large volume irradiation facility has been constructed for this purpose. A systematic effort has begun to make accurate and efficient measurement of trace elements in human serum, focused initially on zinc and selenium. The crucial step of valid sampling of biological materials was reviewed in a special issue of the Bureau's Journal of Research (1).

The strong interaction with industrial scientists using neutron depth profiling, prompt gamma activation analysis, and neutron activation analysis is continuing with a growing number of guest workers, research associates, and joint publications. The long-term NDP study of the mobility of helium in nickel has been completed. The measurement of distributions of lithium and boron in metals, glasses, and polymers continues to produce important results.

The joint NBS/FDA/USDA study of trace elements in human diet, sponsored by the International Atomic Energy Agency, has completed its second year. A total of 30 biologically important minor and trace elements have been measured on the total diet material, USDIET-I. A second composite diet material is being prepared for study and will be considered for use as an NBS Reference Material.

During the coming year, the Group will continue to improve the accuracy and sensitivity of those nuclear methods that are applied to elemental measurement. This will address the problems of sample preparation, irradiation, and counting, with the goal of reducing and quantifying the various sources of systematic error in analysis by nuclear methods. In particular, the application of NAA, both instrumental and radiochemical, to the analysis of important trace elements in biological samples will be pursued. In the area of materials analysis, the improvement of both the beam techniques, NDP and PGAA, and traditional NAA will extend our capabilities in sensitivity, and the number of elements that can be profiled or measured. As always, one of the major products of all of our efforts is the increased capability to carry out certification measurements on Standard Reference Materials.

Ronald F. Fleming, Group Leader; Thelma A. Allen, M. James Blackman, Donald A. Becker, B. Stephen Carpenter, Kevin D. Diamant, R. Gregory Downing, Kathleen A. Fitzpatrick, Robert R. Greenberg, G. Venkatesh Iyengar, John K. Langland, Richard M. Lindstrom, George J. Lutz, John T. Maki, Bruce R. Norman, Susan F. Stone, Mano P.M. Tillerkeratne, and Rolf L. Zeisler.

(1) Journal of Research of the National Bureau of Standards 91, No. 2, March 1986 Special Issue: Biomedical Sampling.

B. Selected Technical Reports (Inorganic Analytical Research Division)

1. Installation of an Automatic, Multi-Collector Mass Spectrometer

I.L. Barnes and J.W. Gramlich

An automatic thermal ionization mass spectrometer has been received, installed and initial analyses have been completed. The instrument has provision for loading of up to 13 samples at one time with full computer controlled operation possible. The most important feature, however, is that the instrument is equipped with 7 deep Faraday cup collectors, 6 of which are externally adjustable. This permits simultaneous collection of up to 7 mass beams. This collection scheme is made possible by the unique ion optical design of the instrument which takes advantage of the fact that greatly increased dispersion is obtained when ions enter the magnetic at an angle other than normal to the field. By use of this design, the instrument with a nominal radius of 23 cm has the equivalent dispersion of a 46 cm radius magnet. Additional optical magnification at the collector gives this instrument dispersion equal to that of a mass spectrometer with a 64 cm radius, sufficient to permit deep Faraday cup collectors that can be adjusted to cover the mass range from 2 to 240.

Installation and acceptance testing was completed in early July and while there has been insufficient time to complete extensive tests of all the capabilities of the instrument, some excellent data has been obtained. Isotopic analyses of about 40 samples of neodymium have been completed with very good results. For example, external (run to run) precision of a set of 13 samples of the commonly used "La Jolla" neodymium standard was 9 ppm and equal or better precision was obtained on other materials. During these analyses it was determined that all 7 neodymium isotopes (which cover the mass range 142-150) could be collected simultaneously. A very important test was made during these analyses to determine that all 7 collectors were collecting ions with equal efficiency and that amplifier drift was sufficiently small during the course of the analyses that the results were unaffected. This was done by collecting several specific ion beams in a particular set of cups and then shifting these same beams to a different set of cups. Within a few (1 to 4) ppm, no differences could be detected in the ratios measured or in the uncertainties.

In addition, a new determination of the atomic weight of strontium has been completed. The 6 synthetic mixes of the separated isotopes of ^{88}Sr and ^{86}Sr that were used in the original determination of this atomic weight (1) were each remeasured 6 or 7 times. These analyses were interspersed with the analyses of 19 samples of SRM 987, Strontium Carbonate. While the statistical analysis of the final data has not yet been completed, preliminary results indicate that the atomic weight of strontium is 87.6167518 ± 0.0000735. This result is within the uncertainty of the previously determined value but the uncertainty is reduced by a factor of 2. A paper describing this work is in preparation. Perhaps the most important thing determined during the course of this work, is that in the original work the final total uncertainty was about equally divided between the chemical preparation and the mass spectrometric measurement of the ratios while, in the new determination, the final uncertainty is essentially all due to the chemistry. This means that in future work the ultimate precision obtained may be limited by our ability to prepare samples.

The early work with this instrument has indicated that, to take advantage of the much increased precision, new filament preparation, loading, and drying procedures will have to be developed for each element and work has started on these procedures. We plan early development work on procedures for nickel to use the instrument for measurements of the atomic weight of this element.

2. The Determination of Lead Isotope Ratios in Some Ancient Objects

I.L. Barnes, E. Joel (Smithsonian Institution), and R.H. Brill (Corning Museum of Glass)

The measurement of the isotopic ratios of lead in ores and slags from sites known to have been in use in ancient times and in ancient objects can often be used to determine or confirm the provenance of these objects. Since three of the four lead isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) are the stable end product of the radioactive decay of uranium and thorium, the isotopic ratios of each lead deposit depends on the relative amount of each of these elements present and the length of time of the formation of the lead before separation and deposition of the lead. In theory, each lead deposit has a unique isotopic signature which can be matched with that in the objects of interest.

In the past year, the long term cooperative project with NBS, the Smithsonian Institution and the Corning Museum of Glass has continued with high precision isotopic analyses of lead from a number of objects and ores. One of the projects involved the analyses of a number of objects taken at a site under excavation in San Salvador known as the "Long Bay Site". There is much current speculation that this is the site of the first landfall made by Columbus on the discovery voyage. European made objects such as coins, pieces of metal (that may have been a shoe buckle) and a number of glass beads of a type commonly used as trading gifts have been recovered from this site. Lead isotope analyses as well as other examination are all consistent with a spanish origin or source for these samples at about the time of the Columbus voyage.

Lead isotope analyses have been completed on essentially all of the chinese bronzes from the Sachler Collection to be housed in the new Smithsonian Museum now under construction. Since few samples of ores from sites in China known to have been used in ancient times are available at this time, we have not yet been able to identify possible sources of raw materials for these objects though we believe this is possible in the future. The data have however been of great use in refining the lists of stylistic attributes used to identify objects from particular periods.

We have also obtained samples from recently rediscovered sites of ancient mining activity in central Turkey. These lead samples are of particular interest since they contain rather high concentrations of silver, gold, and in a few cases, cobalt. Cobalt is known to have been used in early times as a colorant but sources of cobalt in the middle east are quite rare. It is also hoped that information will be obtained of possible sources for the many objects made and traded in ancient Persia.

3. Ultratrace Elemental and Isotopic Analysis of Os and Re Using RIMS and Thermal Vaporization

R.J. Walker and J.D. Fassett

The capability of precisely measuring the isotopic compositions of sub-nanogram quantities of Re and Os in geologic materials is of great potential value to geochemists examining the chemical evolution of the earth and solar system. The Re-Os isotopic system is based on the radioactive decay of ^{187}Re to ^{187}Os with a half life of 4.35×10^{10} yr. Since the geochemical behavior of Os is unique, the Re-Os isotopic system can provide complementary information to other isotopic systems (Sm/Nd, Rb/Sr, U/Pb) which are now used to study the chemical evolution of the earth's mantle and crust. Both Re and Os generally occur in sub-ppb concentrations in geologic materials and, thus, a technique is required that is capable of routinely measuring sub-nanogram quantities of both elements.

Resonance ionization mass spectrometry (RIMS) is a technique that combines the ability of laser radiation to selectively and efficiently photoionized gas phase atomic species with the mass resolution capabilities of mass spectrometry. A number of other mass spectrometric techniques have been and are being investigated to make isotopic Os measurements. To date, however, the physical and chemical properties of Os have combined to forestall the routine application of these other techniques to sensitive and accurate Os isotopic measurement.

We have developed RIMS procedures for the sensitive measurement of Os and Re isotopic ratios. Efficient thermal atomization and resonance ionization has necessitated the development of specialized sample loading techniques. The Re and Os are preferentially adsorbed onto resin beads, which separates them from other elements that may remain after chemical processing. These resin beads are carefully placed on microfilaments with graphite and collodion, which facilitates the chemical reduction of these elements in the mass spectrometer. The resin bead loading produces a virtual point source of atomization from the hottest part of the filament. The microfilament is pulse-heated, which maximizes sample utilization: the duty cycles of atomization and ionization are matched and the required high temperature for atomization is easily maintained.

Three types of measurements have been conducted in order to define the precision, accuracy, and sensitivity of the RIMS measurement system for Re and Os: 1) measurement of isotopic compositions of microgram quantities of spikes and standards, and mixtures of both, 2) measurement of loading blanks, and 3) measurement of sub-nanogram quantities of standards. The measurement of microgram quantities of mixed isotopic solutions indicate precisions and accuracies of 1% can be achieved for both elements. Loading blanks have been examined for a number of different filament substrate materials. These loading blanks are determined by the direct loading of isotopic spikes onto filaments in the same manner of samples (500 and 50 pg of ^{185}Re and ^{190}Os, respectively). The blanks ranged from 2 ng to 3 pg for Re and 260 pg to 3 pg for Os. The reproducibility of the system for the determination of sub-nanogram quantities was assessed by multiple runs with 900 pg quantities of Os standard loaded on the filament. The ^{192}Os/^{190}Os ratio was measured with 1.3% relative standard deviation; the ^{187}Os/^{186}Os ratio was measured with a 3.2% relative standard deviation. The precision of measurements was counting statistics limited.

The making of real measurements at the highest sensitivity forces the solution of many problems that are not evident in the analysis of larger amounts of material. Here we have used RIMS to correct for the non-selective ionization of a hydrocarbon background. This correction reduces the effective sensitivity of the instrument, because the ultimate limitation will be the signal-to-background ratio. A second problem was observed due to the accidental overlap of photoionization wavelengths of Os and Ta filament substrate. This overlap resulted in a scatter background for Os from ^{181}Ta. Clearly in the development of RIMS schemes, sensitivity is only one consideration. Selectivity must be evaluated relative not only to obvious isobaric overlaps, but also to ionization of species that can degrade the overall measurement process. Chemical separation procedures for Os and Re from rocks is presently being developed and initial analyses being made.

4. Quantification of Pulsed Ion Currents Produced in Resonance Ionization Mass Spectrometry (RIMS)

J.D. Fassett, R.J. Walker, J.C. Travis, and F.C. Ruegg

The use of pulsed lasers as ion sources in inorganic mass spectrometry creates a new challenge for precise and accurate isotope ratio measurements. Although pulsed laser ionization processes can be orders of magnitude more sensitive than traditional, continuous ionization techniques such as thermal ionization or electron bombardment ionization, the problem of quantitation of pulsed ion signals has not been adequately addressed. Furthermore, the measurement of ion currents over relatively large dynamic ranges (> 1:10^6) is a non-trivial problem in pulsed ionization. Laser ionization can result in the formation of ion packets as large as 10^5 ions/pulse/mass that are accelerated and focussed to the detector with time spreads as small as 10 ns. Issues of detector response linearity between and among differing species at widely different intensities must be faced in order to demonstrate quantitative isotope ratio measurement.

In last year's annual report we described the development of a measurement system based on time array detection using a transient digitizer. Here, we report on the evaluation of this system. We have evaluated the linearity of the response of the electron-multiplier-based ion detector and developed procedures for large dynamic range ratio measurement. Data have been collected which demonstrate quantitative ratio measurements in pulse counting/pulse counting mode, pulse counting/analog mode, and analog/analog mode of operation.

The laser-generated ion signal is detected using a 17-stage electron multiplier whose output is preamplified and directed into the transient digitizer. A non-symmetric pulse with a half-height width of 2 μs is output by the preamplifier. The transient digitizer is set up to sample 2048 channels, 20 ns per channel, and is triggered by a photodiode detector of the laser ionization pulse.

Several routines were developed for processing of data acquired by the transient digitizer in real time, so that no ionization data is sacrificed. The most general routine signal averages the digitized waveforms acquired by the transient digitizer. In addition to the signal averaging that is done, a pulse-counting routine has been incorporated into the general signal processing program which is used for low level signals. At high signal levels this routine is not useful for quantitation but can be used to verify that there have been no pulses that have exceeded the 8-bit dynamic range of the digitizer. After the signal-averaged data has been acquired and processed, five pieces of information are extracted, displayed, and transferred to the isotope ratio program: 1) total number of waveforms acquired; 2) position of peak; 3) baseline; 4) baseline corrected signal; and, 5) number of pulses detected.

The isotope ratio program controls the laser wavelength, magnetic field of the mass spectrometer, and data acquisition and processing. The program is a variant of the standard ratio program used in high precision thermal ionization where a single channel detector is available and alternating measurements are made on two isotopes. The key change that was made to accommodate RIMS is the determination of baseline on mass for each isotope, but off the resonance wavelength. Thus, the signal quantified is the elementally selective ionization caused by the laser.

The measurement of Os and Re using this system has been described in another highlight of this report. Those measurements were made at one gain setting of the electron multiplier and both intensity-averaged and pulse-counted ratio measurements were demonstrated. Procedures have also been developed for large ratio measurements which combine pulse-counted and intensity-averaged signals at different gain settings of the electron multiplier. These procedures were tested by measuring natural $^{184}Os/^{192}Os$ which has a ratio of $4x10^{-4}$ and an isotopic standard of $^{129}I/^{127}I$ which had a ratio of 10^{-6}.

The predominant uncertainties in ratio measurement will differ according to the signal quantification scheme: for large signals, the linearity of the transient digitizer and reproducibility of the mass spectrometry is limiting; for small signals, pulse counting statistics predominate; and, when the two schemes are combined, gain calibration of the multiplier is significant. Nonetheless, our RIMS measurement system has proven to be quantitative over a large dynamic range of measurement.

5. Detection of Uranium from Cosmos-1402 in the Stratosphere by Thermal Ionization Mass Spectrometry

W.R. Kelly, J.D. Fassett, R. Leifer (DoE), and Z.R. Juzdan (DoE)

Cosmos-1402, a Soviet radar reconnaissance satellite powered by a nuclear reactor containing about 50 kg ^{235}U, was launched into an earth orbit of 240-270 km on August 30, 1982. A malfunction on December 28, 1982 prevented the reactor from being boosted into a burial orbit and on February 7, 1983 it reentered the earth's atmosphere over the South Atlantic Ocean. In an effort to determine the fate of the reactor, the $^{235}U/^{238}U$ ratio of the aerosol in the stratosphere has been measured by mass spectrometry. This U isotopic ratio is a particularly sensitive tracer for the kind of event because the natural ratio is small and constant, 0.0072, whereas that of the fuel for a reactor of this type is about 10.

Since balloon launches and sampling were restricted to the northern hemisphere, it was necessary to wait until stratospheric circulation transported the reactor aerosol into the northern hemisphere and to lower altitude before sampling. Based on 1983 meteorological observations, it was estimated that the best time for sampling would be late winter of 1983. One balloon was launched on February 28 and another on March 13, 1983, providing samples between 27 and 39 km (see Table 1). A flight 16 days before the reentry of

Cosmos-1402 provided an important background sample which permitted measurement of the concentration of U nuclides in the stratospheric aerosol prior to the burn-up of Cosmos-1402. Aerosol samples were collected on IPC-1478 cellulose filter paper in samplers designed and used in the Department of Energy's (DOE) project ASHCAN. Portions (~10 g) of filters were spiked with ^{233}U, wet ashed, chemically purified by anion exchange, and the U isotopic ratios measured by thermal ionization mass spectrometry using pulse counting detection. Chemical yields were determined for all samples and the appropriate blank corrections were applied to both the concentration and composition data.

Table 1. Filter Samples Collected in the Study of Cosmos-1402

Filter No.	Sample Date	Altitude (km)	Volume of Air Sampled (m^3)	Comments
1,2	--	--	--	Blank for 6
3	--	--	--	Blank for 7,8
4	--	--	--	Blank for 5
5	1/23/83	38.6	40.5	Background
6	2/28/84	36.0	92.4	Post-Cosmos-1402
7	3/13/84	26.6	60.5	Post-Cosmos-1402
8	3/13/84	31.9	17.9	Post-Cosmos-1402

Table 2 gives the concentration and composition data. The blank filters show a small enrichment of ^{235}U compared to natural U. This was also observed in a previous study, but the exact reason for this is unknown. The filter material used in this study was about an order of magnitude more homogeneous in U concentration than that used previously, which permits smaller perturbations in U isotopic composition to be detected. Of the three post Cosmos-1402 samples, only filter 6 shows a measured isotopic enrichment above the mean of the blank filters. Although filters 7 and 8 do not show evidence of enrichments above the blank levels, the following model allows the decoupling of the large amounts of natural U that were collected at the lower altitudes and the determination of the enriched U from the reactor component.

The following mass balance relation can be written for each filter:

$$(^{235}U/^{238}U)_m = \frac{(^{235}U)_b + (^{235}U)_r + (^{235}U)_a}{(^{238}U)_b + (^{238}U)_r + (^{238}U)_a} \qquad (1)$$

Table 2. Uranium Isotope Composition of Filter Samples

			Atom % (±2s)*			
	Filter Weight	Atoms ^{238}U per g	^{234}U	^{235}U	^{236}U	^{238}U
No. #	(g)	(10^{10})	(10^{-4})	(10^{-3})	(10^{-4})	
			Natural Uranium			
			55	720	0	99.28
			Cosmos-1402 Reactor			
			10000	90000	5000	8.5
1(1)	4.2430	47.1±0.7	85±20	845±10	3±6	99.150±0.0010
2(2)	4.3307	48.5±0.8	106±29	832±18	5±6	99.160±0.0018
3(1)	6.1505	43.1±0.4	79±11	832±28	2±4	99.180±0.0028
4(1)	8.1178	46.8±2.0	80±31	834±5	0±3	99.160±0.0005
		Pre Cosmos-1402 Stratospheric Aerosol				
5(9)	37.1756	60.7±1.4	94±3	815±2	8±3	99.170±0.0002
		Post Cosmos-1402 Stratospheric Aerosol				
6(11)	44.5520	76.8±1.6	96±6	942±4	19±1	99.030±0.0004
7(2)	3.4602	211.0±2.0	69±4	800±7	2±5	99.192±0.0007
8(2)	5.4806	113.0±2.0	101±10	827±6	11±3	99.160±0.0006

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*The total uncertainty includes components from ion counting, blank, and chemical yield.

#Number in parenthesis represents number of determinations. When the number is greater than 2, the atom % and ^{238}U concentration are the weighted mean and standard deviation. 42% of filter 5 was analyzed. 34% of filter 6 was analyzed.

$Assumed to be similar to NBS/SRM U-900.

where m, b, r, and a stand for measured, blank, reactor, and air respectively. Since we have a good estimate of the ^{235}U and ^{238}U concentrations in the blank filter, we can calculate the concentrations of these isotopes in the natural background aerosol and the reactor derived aerosol. We have assumed the $(^{235}U/^{238}U)_r$ ratio to be 10.6; however, this assumption is not critical for the calculation of the $(^{235}U)_r$ concentration. A ratio as low as 0.1 would not change the calculated concentrations. By assuming that background filter 5 is a two component mixture of filter blank and ambient aerosol, we calculate the $(^{235}U/^{238}U)_a$ ratio to be 0.00755±0.00052 (2s) which is indistinguishable from the natural U ratio of 0.0072 and indicates that the stratospheric aerosol had a natural $^{235}U/^{238}U$ ratio. This latter value was used for the air component in equation (1) for filters 6, 7, and 8.

The average mass of Cosmos-1402 ^{235}U per gram of filter 6 is $1.2\pm0.2\times10^9$ atoms or a total amount for the filter of 68 pg ^{235}U. This corresponds to an excess in ^{235}U of 36±9% relative to natural U. The maximum observed ^{235}U enrichment for Cosmos-1402 was significantly less than that observed for Cosmos-954. This is ascribed to the higher altitude of injection and later sampling time which caused a greater dispersion of the material. Assuming that the ablation aerosol is distributed uniformly around the earth above 26.6 km, we calculate the total mass of ^{235}U injected into the stratosphere to be 30±8 kg. This value is close to the reported reactor mass of 50 kg ^{235}U and suggests that all excess ^{235}U in the upper atmosphere could have come from this one reactor.

6. Progress in the Development of Microwave-Coupled Acid Dissolution Procedures

H.M. Kingston and L.B. Jassie (CEM Corporation)

The method of microwave-coupled acid dissolution of samples has gained enthusiastic support from industry and researchers alike and their desire for more fundamental data to aid their understanding of the parameters governing the process has continued. Over 250 industries, universities, research laboratories or other government laboratories have contacted the NBS for information and guidance in microwave dissolution technology.

One of our contributions to help meet this research and information need is the publication of our studies to date on closed vessel microwave digestion. This report will be published in October as a paper in Analytical Chemistry. This paper describes methods of predicting the final temperature and time to temperature at any power setting for single component acid systems. It also gives examples of reaction control methods and examples of digestion procedures for some of the most popular biological and botanical Standard Reference Materials.

During this past year, we have cooperated with several other federal laboratories in the application of the microwave technique to problems confronting these organizations. I.E. DuPont Savannah River Laboratory requested our help in developing a digestion procedure for five materials which simulate the nuclear waste tank contents and their mixed process materials during the making of nuclear waste glass. A timely sample digestion procedure which can be performed remotely is very important in their quality control efforts. We were successful in developing a single procedure that digested all five materials. The first step relies on a 10-12 minute microwave digestion with hydrofluoric and nitric acids under 5 atm of pressure and exceeding 170 °C. As part of this program, a fiber optic temperature measurement system was evaluated for monitoring temperature in microwave fields and found to possess many advantages over previous temperature measuring devices. A paper will be forthcoming on this procedure.

The analysis of biologically active inorganic elements is of importance in diverse studies of medicine, nutrition, and agriculture. Currently, we are concluding studies with the Department of Agriculture and have proved that biological fluids and tissues containing Se can be digested in closed vessels in the microwave without losses of this volatile element. Losses in the sample preparation step are one of the most frequent causes for erroneous Se concentrations reported in biological materials. The studies include endogenously labeled Se-75 and Se-82 that were monitored using gamma-ray spectroscopy and GC/MS respectively. A paper will be forthcoming on this procedure.

We are organizing the first symposium on microwave sample preparation which will be held at the Eastern Analytical Symposium in October 1986. This symposium will act as a focus for fundamental methods in all the major sample types currently prepared by microwave dissolution: biological; environmental; geological; and selected industrial samples.

Further efforts to define parameters are progressing and include studies of new acids and new materials. Specific anomalies between accepted theory and measured phenomenon are being studied to understand the fundamental relationships of materials and the absorbed energy which produce these effects.

7. Inductively Coupled Plasma Mass Spectrometric Analysis of Major and Trace Elements in SRMs Using Isotope Dilution

P.J. Paulsen and E.S. Beary

The ICP-MS now has detection limits as low as 0.2 ppb for water samples using a one minute data collection period covering a mass range from m/z 2 to 250 (an all element survey). Analysis of SRMs with the ICP-MS is done using isotope dilution analysis since it is an inherently accurate technique. A major advantage is the ability to make precise isotope ratio measurements even under conditions where the absolute signal level is unstable. Over forty elements can be analyzed by isotope dilution using the ICP-MS.

Major Elements in SRMs

The ICP-MS has a higher sample throughput rate when compared to other mass spectrometric methods used for isotope dilution. However, to take advantage of its speed, comparable time savings must be made in the chemical processing steps of an isotope dilution analysis. Analysis of major elements by ICP-MS-ID can provide faster chemistry since it doesn't need the chemical preconcentration or separation steps required by other MS-ID methods. Better precision and accuracy are expected for major elements than for trace elements and this is the critical factor for ICP-MS-ID.

An ICP-MS-ID analysis of six copper concentrate samples was compared to an independent thermal MS-ID analysis of the same material. A sample by sample comparison between the two MS techniques showed an average difference of 0.33%. Most of this difference can be attributed to changes in the ICP-MS "mass bias" correction factor which showed a ±0.24% rsd during the data collection period.

Pb in reference fuel by ICP-MS-ID found 768±8 ppm (1σ) as compared to a value of 767.3±1.5 ppm (1σ) measured by thermal MS-ID. Again it was found that variation in the "mass bias" correction factor could explain the scatter in the results. Possible sources of variation in the "mass bias" correction are under investigation.

Trace Elements in SRMs

Analysis of a Ni-Cu alloy, SRM C1248, illustrates the capabilities of ICP-MS-ID for trace element measurements near detection limits. Tin and lead determinations were required when co-operating laboratories reported divergent results, over a factor of ten for Sn, at low ppm levels. Preliminary tests on the sample indicated that it could be measured without preconcentration or separation chemistry. One gram samples were spiked with ^{117}Sn and ^{206}Pb, dissolved and equilibrated, then diluted to 100 mL with 1% HNO_3. The ICP-MS "sampling cone" quickly clogged up with this "1% solids" solution. A dilution of 1 g/L was required before the ICP-MS interfacing "sampling cone" could operate properly. Tin with a ppm concentration in the original sample, was therefore at a ppb in the solution being introduced into the ICP. In the parlance of "ICP-MS" vocabulary, this would normally be referred to as a ppb of tin. This distinction between concentrations in the original sample and the "concentration" introduced into the ICP because of instrumental constraints is not often made in promotional information and literature.

Our analysis found 1.09±0.15 μg/g (2σ) of tin and 3.84±0.16 μg/g (2σ) of lead in C1248. Dilution of 1 g to 1 L resulted in a signal to noise ratio for tin that is as low as is practical for certification of an SRM. Analysis of lower concentrations would require preconcentration techniques and would result in both better precision of analysis and lower detection limits.

8. Improved Laboratory Facilities for Trace Element Determination

J.R. Moody

Since 1971, a Class 100 or better clean laboratory has been an essential part of the mass spectrometry group's trace metal analysis methodology. The laboratory, built in 1971, was the first attempt at clean room design by NBS staff and some shortcomings were evident after a few years of use. All subsequent versions of this laboratory have incorporated various upgrades which either eliminated or greatly diminished the unwanted effects.

In recent years, the effects of corrosion and poor ventilation had rendered the original (1971) clean lab almost unusable for trace metal analysis even though the particle counts were still acceptable. At the same time, Division 553 was finding that the use of a clean bench for certain of their micro-analytical analyses was less than satisfactory. Eventually a decision was made to dismantle the old clean lab and build a new facility for both groups.

This facility was finished in early March 1986 and after acceptance tests and adjustments is now considered to be fully operational. The present design is somewhat different from earlier designs, in that no interlock, corridor, or change room exists between the hallway of the building and the clean laboratory. This compromise allowed the incorporation of 25% more usable laboratory space in the same room, an important consideration when a shared facility is being designed.

The portion of the laboratory used by Division 553 is walled off by plexiglass partitions to form a completely independent pressurized facility. Neither laboratory's functions can have an adverse effect upon the other. The design goal was to meet a Class 10 standard under all conditions of usage (e.g., with a door open). The recently completed performance tests indicated that all clean bench locations and each of the 3 laminar flow fume hoods met a Class 1 or 2 standard. This result is largely attributable to higher quality HEPA air filters and a higher percentage of recirculated air.

The other noteworthy feature incorporated into the laboratory is a PVC and fiberglass fume hood imported from England for use as an acid bath-clean up station. For the first time, the group now has a facility for acid washing where there is no chance of metal contamination, and, equally important, there is minimal risk to the laboratory because of escaping acid fumes. Laboratory ventilation is now very good to excellent.

The Class 1 performance may not be an important factor in contributing to lower analytical blanks. However, the present design incorporates all of the lessons learned in clean room use and design at NBS and should far out-last and out-perform previous versions. The total cost for the project as completed was $105 K, well below current commercial costs for a Class 100 room of similar size and fittings.

9. Development of a Computer-Controlled System for Analytical Separations by Column Chromatography

H.M. Kingston and F. Ruegg

The first phase of a multi-year effort to develop an automated chemical separation system has been completed. This phase consisted of system design, equipment assembly and testing. Some new equipment was developed to perform unique tasks. The logic and control programs for the application are currently under development.

This system will perform chelation and ion-exchange separations which isolate single trace elements or groups of elements from their sample matrix. It will be used to support thermal isotope dilution mass spectrometry which requires the isolation of each element prior to instrument introduction. Other instrumental groups in the division will also be supported through the separations by reducing instrumental interferences from matrix elements.

The system is unique in its design and concept. It relies on robotics for the necessary movement of beakers and reagent dispensing. Actual chemical handling is accomplished through the use of computer controlled valves. The control of the entire chemical separation procedure is handled by a personal computer that programs the robot and valves automatically. The robot controller is used to store subroutines that are organized and then called in order by the computer. This is a conceptual departure from standard laboratory robot applications.

This system has been designed as a multi-separation system. It is designed to be a dynamic growing instrument which can learn new tasks that can be integrated into its separations procedures. These procedures can be performed any number of times and in any sequence depending on the analyst's requests. The format of the separation can be altered by the analyst for individual sample set without reprogramming the robot. The reprogramming will be done by the computer automatically after the chemist alters the separation parameters.

The system will perform many different separations which are repeated many times in the course of yearly elemental determinations. In addition, it will be capable of running separations which are now not widely used due to their long time requirements and inability to be divided into manageable components. Additional separations will be added in the future which will increase the automated separations available to the analysts.

10. Use of Voltammetry to Detect Electroactive Organic Products from Microwave-Assisted Wet Ashing

K.W. Pratt and H.M. Kingston

Microwave-assisted dissolutions of biological samples have received significant attention due to their improved rapidity and ease of control as compared to classical digestions at atmospheric pressure. A critical factor in the evaluation of these dissolutions is the completeness of decomposition of the original matrix. Research during the past year has demonstrated the capability of voltammetry to indicate the effectiveness of microwave-assisted dissolutions of biological samples.

Microwave-assisted dissolutions generally employ HNO_3 alone or a HNO_3-HF mixture as the solvent. For biological samples, the expected products of incomplete dissolution include nitro compounds. This is particularly true for components of the sample containing benzene rings or other aromatic structures, which are highly resistant to decomposition. The resulting nitro compounds are generally electroactive and therefore may be detected polarographically. Evidence for such compounds was obtained during development of a procedure for the polarographic determination of trace metals in SRM 1577a, Bovine Liver. Polarograms obtained using microwave-assisted dissolution in HNO_3 + HF without $HClO_4$ contained peaks at -0.23, -0.34, and 0.75 V vs. Ag/AgCl reference, in acetate buffer. These peaks did not correspond to metals known to be present in the sample. In addition, results obtained for Cu in these samples were lower than the certified value. Further experiments demonstrated that these unwanted peaks were eliminated or greatly reduced if the digested samples were refluxed with boiling $HClO_4$, which destroys any organic species not decomposed by HNO_3. Results found for Cu using $HClO_4$ agreed with the certified value. Results obtained for Zn both with and without use of $HClO_4$ were in agreement with the certified value.

The unwanted peaks occur at potentials characteristic of nitroaromatic compounds (-0.2 to -0.5 V) and aliphatic nitro compounds (-0.7 to -0.9 V) at this pH. Residue from the initial HNO_3 digestion was found to contain an organic component or components which were insoluble in hexane and cold water but soluble in hot water and methyl isobutyl ketone (MIBK). Following extraction into MIBK, the organic species could be re-extracted into aqueous NaOH. Polarography of this NaOH extract in acetate buffer yielded a peak at -0.23 V vs. Ag/AgCl. Ultraviolet spectra of the MIBK extract were consistent with the presence of nitroaromatic compounds.

The above data all point toward acidic nitroaromatic compounds as major components of the residue remaining after incomplete digestion of biological samples in HNO_3. Based on experimentally-obtained polarographic half-wave potentials, the most likely compounds responsible for the peak at -0.23 V are o-, m-, and p-nitrobenzoic acids. These compounds are plausible products of incomplete oxidative degradation of a biological matrix using HNO_3. The other peaks at more negative potentials likely result from other, non-acidic nitro compounds. Investigations using HPLC with UV and electrochemical detection are currently in progress to obtain further information about the products of incomplete digestion of biological samples.

The sensitivity of voltammetric analyses to organic complexing agents is demonstrated by the low values and poor precision obtained for Cu in digestions using HNO_3 alone. Because of this sensitivity, voltammetry can serve as an excellent indicator for complete decomposition of organic sample matrices. High precision for voltammetric determinations, coupled with the absence of voltammetric peaks not associated with trace metals, indicates complete decomposition of the sample matrix.

11. Absolute Measurement of Aqueous Electrolytic Conductance Standards

Y.C. Wu and W.F. Koch

Measurements of aqueous electrolytic conductance are performed routinely in a variety of disciplines and industries. Conductivity is a measure of the ionic content in solution and thus has applications in pharmaceuticals, power plants, rainwater, lake surveys, and oceanography, to name a few. The need for standards for this measurement is immediate and work in the Electroanalytical Research Group has begun to meet this need. A thorough review of the measurement of and standards for aqueous electrolytic conductance has been completed. At present, the standards considered to be the most precise and accurate have been set forth by the International Organization of Legal Metrology (OIML), and have been adopted by most standards organizations including ASTM. However, the uncertainty assigned to these standards, especially the secondary standards, is somewhat larger than would be expected from the physical aspects of the measurement. It has been deemed necessary to investigate this deficiency before issuing NBS standards which would propagate this uncertainty.

Specific conductance is the reciprocal of resistivity. Thus, through resistance, it may be defined as $K = G/R$, where G is the ratio of l/A (called the cell constant), and R is resistance. G is defined in terms of the lines of force traveling the distance (l) between the two electrodes over the effective cross-sectional area (A) of these lines of force between the two electrodes. Hence, the units of K are $ohm^{-1}cm^{-1}$, or in SI units, S/m (siemens per meter). To measure specific conductance on an absolute basis, both G and R must be determined independently and on an exact (i.e., physical) basis. The measurement of R has been accomplished through the use of a Jones' Bridge, calibrated by the Electricity Division at NBS. One approach to the attainment of G would be the accurate measurements of l and A. Because of the geometry and design of the conductance cell, these would be exacting and non-trivial measurements to the accuracy required. Instead of this direct determination of l and A, a substitution method has been devised using a conductance cell of unique design. The cell is similar to a Jones' cell, except that a portion of the distance between the electrodes is now variable by the insertion of precision-bore borosilicate glass tubes of accurately known diameter and varying, but accurately known, lengths. It was a major engineering accomplishment to construct a leak-free cell and required several modifications.

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 for the NBS cell: A_o, the area, due to the portion of the cell between the electrodes and the connecting flanges; and A_i, due to the diameter (hence, the area) of the replaceable center tube. A_i must be accurately known and the diameter of the center tubes must be identical to that of the connecting tubes of the body of the cell. The distance, l, has two components: l_o, the portion of 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, A_o, and the conductivity of a given electrolyte; and r_i, due to the i'th center tube. Thus,

$$R_1 = r_o + l_1/KA_1 \qquad (1)$$

and,

$$R_2 = r_o + l_2/KA_2 \qquad (2)$$

By performing the experiment with two center tubes of different lengths and with $A_1 = A_2$ and by solving the simultaneous equations, K can be determined.

Preliminary experiments using potassium chloride have been completed successfully. Agreement with the OIML recommended value is within 0.02%. Refinements to the cell and the procedure are being made to improve the accuracy and precision, and will be completed in the coming year. This will establish a new basis for all electrolytic aqueous conductivity standards and represents the first high-accuracy endeavor in this field in over fifty years.

12. High Ionic Strength pH Standards Research

Y.C. Wu, R. Roy, and W.F. Koch

The influence of ionic strength on the value of pH and on the measurement of pH is a well-known, but poorly appreciated phenomenon. The recent work of the Electroanalytical Research Group in the measurement of pH in acid rain of low ionic strength gave clear evidence of the erratic nature of this measurement when the customary buffer standards of moderate ionic strength were used to calibrate the conventional glass/reference pH electrode systems. This difficulty was attributed partly to the difference in ionic strength between rain water and the buffer standard, and partly to the asymmetry of the liquid junction potential. It was satisfactorily resolved through the issuance of strict measurement protocols and a control standard, SRM 2694, Simulated Rainwater, which approximates the matrix and ionic strength of rainwater. Attention has now turned to the equally vexing problem of pH measurements in high ionic strength solutions, such as encountered in biological fluids and seawater. The approach being investigated is similar to that used for acid rain, i.e., match the ionic strength and matrix of the standard with that of the solution to be measured.

To develop high ionic strength pH standards, a firm understanding and basis in two fundamental areas must be attained: the activity coefficient as a function of ionic strength, and the influences of neutral salts and of organic compounds on the value of pH. Research in the first aspect is well underway. The approach is to use the Harned cell with dilute solutions of strong acids, such as HCl or H_2SO_4 [around 5×10^{-4} molal (m)] to which neutral salts are added to bring up the ionic strength from 0.1 to 1.0 m. The following electrochemical cell was used:

$$\mathrm{Pt,H_2\ (1\ atm.)} \mid \mathrm{H^+\ (.0005\ m),\ KCl\ (m_2),\ K_2SO_4\ (m_3)} \mid \mathrm{AgCl,Ag}$$

The concentration of KCl (m_2) was varied from 0.005 to 0.02 in order to facilitate extrapolation to zero chloride concentration for the calculation of pH as shown below. The concentration of the neutral salt (m_3) was adjusted to raise the total ionic strength (I) to the desired level. For the first set of experiments, these concentrations were 0.1, 0.17, 0.3, 0.5, 0.7 and 1.0 molal.

The observed emf of the Harned cell, E, was used to calculate pH values as follows:

$$-\log a_H\gamma_{Cl} = (E-E°)/k + \log m_{Cl} \tag{1}$$

where E° and k have their usual significance. Extrapolating $-\log a_H\gamma_{Cl}$ vs. m_{Cl} to $m_{Cl} = 0$ yields:

$$-\log (a_H\gamma)° = p(a_H\gamma)° = pH - \log \gamma°_{at\ I} \tag{2}$$

The quantity $\log \gamma°_{at\ I}$ was evaluated by the Debye-Hückel equation as a function of I with two adjustable parameters i.e.,

$$\log \gamma = -(Az^2\sqrt{I})/(1 + B\mathring{a}\sqrt{I}) + bI \tag{3}$$

where A and B are Debye-Hückel constants. The ion size parameter, å, and b are the adjustable parameters and are obtained by least-squares fitting. Experiments were run over the temperature range 15 to 35 °C. The experimental results indicate that equation (3) is a well-behaved function, and therefore can be used in the calculation of pH values for high ionic strength pH standards.

The 0.0005 m strong acid, high ionic strength solution (I=0.7) prepared and measured as above was used to calibrate a conventional glass/reference pH measurement system prior to the measurement of the pH of "Copenhagen water" and a simulated seawater solution. These two samples were also measured in the Harned cell. The Harned cell approach is inherently more accurate than the glass/reference electrode system, but is tedious and time-consuming. Furthermore, the Ag/AgCl electrode in the Harned cell is very sensitive to contamination and poisoning from components in real samples. This justifies the use of the less accurate, but more convenient and robust glass/reference system, on the condition that suitable standards are used to calibrate the system. The agreement between the two methods was within 0.02 pH units and is considered excellent. The values obtained for the seawater samples when measured with the glass/reference electrode system calibrated with conventional buffer solutions were biased by several tenths of a pH unit.

Additional research is needed to investigate the influence of organic compounds on pH before high ionic strength buffer standards can be certified and issued. This research will have considerable impact on the measurement of pH in clinical and medical situations. Research is also underway to elucidate the ionic interactions in a multi-component system. Moreover, thermodynamic properties in a four component system, such as free energy, enthalpy, and entropy, are being evaluated. This thermodynamic treatment in a complex aqueous system is the first of its kind.

13. Activation Analysis Using Cold Neutron Beams

R.M. Lindstrom, R. Zeisler, and M. Rossbach (Nuclear Research Center, Jülich, Germany)

The application of neutron-capture prompt gamma-ray activation analysis (PGAA) has been pursued to date at only a few laboratories on a full-time basis, partly because of the need for continuing access to a reactor neutron beam. Irradiation times of several hours are required for most samples in which many elements are to be measured, hence the throughput is low because only one sample can be irradiated and measured at a time. The low sensitivity is not due to a low neutron capture rate, but to a low detection efficiency for the resulting gamma-rays, because of the necessary bulk of active and passive shielding around the detector. Simply moving the detector closer to the sample increases the efficiency, but at the cost of higher backgrounds and other consequences of operating instruments in high radiation areas.

For chemical analysis, the ideal neutron field has the largest possible number of activating particles per $cm^2 \cdot s$ on the sample, and the smallest possible number of interfering particles at the detector. A narrow beam is desirable so that the gamma-ray detector can be moved near the sample and the size of the shielding may be minimized. A guided beam of cold neutrons meets these requirements exactly. The slowest neutrons from the reactor are reflected with high efficiency from the walls of the guide tube, while the fast neutrons and gamma-rays decrease as $1/r^2$ with distance from the source. Therefore, the signal to noise ratio is high. Since the apparatus is not near the reactor and other experiments, the background from these sources is low and there is room between experimental facilities to construct efficient shielding. The capture rate is also higher with cold than with thermal beams. Since capture cross sections for most target nuclei are inversely proportional to the neutron velocity, the same number of neutrons per $cm^2 \cdot s$ at 30 K gives three times the reaction rate as at 300 K.

These expectations have been tested at the recently commissioned ELLA Neutron Guide Laboratory at the FRJ-2 (DIDO) reactor of the Nuclear Research Center Jülich. Samples examined include Standard Reference Materials, and industrial, biological, and environmental specimens as air filters. Synthetic standards were irradiated to study the systematic errors in hydrogen containing matrices and other limitations on accuracy with existing facilities. The main advantages of cold neutron beams were verified in the experiments. The PGAA sensitivity, expressed in counts/s•g, was nine times better than the published sensitivity of the UMd-NBS facility. The hydrogen background in the spectrum of a Teflon sample envelope was 100 μg, four times lower than the better of two major PGAA facilities.

In the analysis of plant and animal tissues, the limiting factor for both the sensitivity and the accuracy of PGAA determinations is the amount of hydrogen in the sample. The strong hydrogen capture gamma-ray at 2223.2 keV is accompanied by a high Compton continuum, making the capture lines of other elements below 1995 keV much less sensitive than they would otherwise be. Active Compton suppression can reduce this baseline substantially. With the high gamma-ray detection efficiency possible with cold neutron beams, the practical limitation on the analytical usefulness of PGAA will be the ability to collect data at high counting rates without distortion. With large Ge detectors coupled with compact high-Z gating detectors, Ge-Ge coincidence counting may cleanly resolve interfering lines in a crowded spectrum. Further enhancement in sensitivity is possible since neutron optics may be used to focus cold neutrons onto a small area. The techniques developed for the microscale electron- and ion-probe analogs of this situation are directly applicable for the formation of two-dimensional images, with millimeter resolution, of the elements which produce prompt radiations under neutron bombardment.

14. The Determination of Chromium-50 in Human Blood and Its Utilization for Blood Volume Measurements

R. Zeisler and I. Young (NIH)

Systematic studies involving the measurement of maternal blood volume increases are needed since subnormal increases have been associated with maternal complications and intrauterine growth retardation in a few instances. To establish a possible link, a new measurement procedure for the maternal blood volume is required that would be accurate enough to determine the relatively small differences between normal/subnormal increases during pregnancy.

Currently, only the radioisotope dilution technique employing chromium-51 (Cr-51) as a label for red blood cells can provide results with a standard error smaller than 5%. However, this technique cannot be used with pregnant women and also would impose severe restrictions on a large scale field study because of the radioisotope involved. Therefore, the Cr-51 radioisotope technique should be replaced by a dilution technique that utilizes enriched chromium-50 (Cr-50) as a label. The Cr-50 can then be determined by instrumental neutron activation analysis or mass spectrometry.

The current investigations focus on the development of an INAA procedure for the determination of red cell blood volumes (RCBV). Although INAA procedures were introduced in the 1970's to measure the stable isotope tracer Cr-50 in several clinical applications, the procedure was not routinely implemented for RCBV determinations. A possible reason for this may be the fact that low level determinations of Cr-50 (a 4.35% abundant isotope of natural chromium) are needed for reliable results. These were unavailable at the time. Recently, the knowledge about sources of contamination and the experience in contamination control has enabled us to determine chromium at naturally occurring low levels in such difficult samples as blood, serum, etc.

Besides the establishment of validated sampling procedures for the clinical blood samples, additional precautions were needed for the stable isotope technique with INAA because of interfering activation reactions and small activities produced. These were resolved with irradiations in highly thermalized neutron fields and background reduction during counting by Compton suppression. The application of the procedures to the measurement of natural chromium in total blood yielded the first results reported by INAA at a consistent low level of < 2.5 ng/mL (0.3 to 2.5 ng/mL) in samples from human volunteers and rhesus monkeys.

Based on the INAA procedure, a new approach to the blood volume measurement via Cr-50 isotope dilution has been developed. It utilizes the ratios of the induced activities of Cr-51 to the iron-59 (Fe-59) instead of the calculation of specific activities or concentrations since the iron concentration in the blood cells remains unchanged during the dilution experiment. This makes the method independent of sample size and irradiation and counting parameters that may add to the uncertainty of the measurements. Only the volume or mass of the labeled blood which is injected into the subject's blood stream for dilution must be known exactly. The dilution factor is then determined on a second blood sample and the volume can be calculated. The estimated uncertainty for this procedures is not exceeding several percent and results may be more reliable than with the classical Cr-51 procedure. A first comparison of the two techniques confirmed this estimate. Due to its simplicity and inherent accuracy and precision, this novel approach is well studied as a clinical tool to study problems associated to the maternal blood volume.

15. Evaluation of USDIET-I Total Human Diet Samples for Nutritional Constituents

G.V. Iyengar (USDA)

A multi-nation study, sponsored by the International Atomic Energy Agency, is aimed at obtaining comparative data on dietary intakes of 25 biologically important minor and trace elements in a variety of developed and developing countries. Three Federal Agencies, namely the National Bureau of Standards (NBS), the Food and Drug Administration (FDA) and the U.S. Department of Agriculture (USDA) are participating in this study. The scope of the study provides an unique opportunity to develop a coordinated approach by the collaborators of these 3 agencies for the U.S. part of the study.

The combined expertise of the participants is aimed toward the needed developments and improvements of analytical methodology for the accurate assessment of the dietary intakes of trace elements. Aspects of quality assurance in sampling, sample preparation, analysis and data evaluation have been addressed by intercomparison studies of minor and trace elements in dietary reference materials (NBS Rice Flour SRM 1568a, NBS Wheat Flour SRM 1567a and two mixed diet samples, namely IAEA-H9 and TDD-1D) using different analytical techniques. Precision and accuracy aspects related to Flame Atomic Absorption Spectrophotometry, Atomic Emission Spectrophotometry with an inductively coupled plasma source and Neutron Activation Analysis were evaluated by analyzing the same test materials by all the three methods.

As a contribution to this project, a benchmark mixed U.S. diet research material using 201 different foods from the FDA Total Diet Study (TDS) has been prepared. According to the FDA-TDS study, a 25-30 year old male consumes daily a total of 3075 g from these 201 foods. This represents the group with highest caloric intake per day and has been used as a basis for all the calculations in the present study. The first batch comprises about 10 kg of mixed diet.

Proximate analysis has been carried out on USDIET-I (fresh material) and the following results were obtained; total volatiles = 83.8%, ash content 0.66%, fat = 2.92%, protein = 3.42%, carbohydrates = 9.2%, and total caloric energy (kcal/100 g) = 76.76.

Over 30 minor and trace elements have been characterized in USDIET-I using a combination of analytical techniques. A comparison of the daily intakes of Ca, Cu, Fe, Mg, Mn, Na, P, and Zn from this total diet material with those of FDA-TDS figures calculated from single food analysis results showed that the mixed diet concept is a viable approach. The daily intakes from USDIET-I were also compared with the Recommended Daily Dietary Allowances suggested by the National Academy of Sciences. The agreements were generally very good. Additionally, analysis for a number of elements such as Cd, Cr, Hg, and Mo that occur at low concentration levels in individual foods, demonstrated the feasibility of a reliable assessment of their daily intake by use of a total diet material, e.g., USDIET-I.

A number of organic nutrients have also been determined in USDIET-I, and their stability during storage is being evaluated. The initial findings suggest that USDIET-I may also be useful to develop reference materials for organic nutrients. There is a great need for these types of reference materials. Thus, it may pave the way for considering production of a single SRM certified for both organic and inorganic nutrients.

Simultaneously, the long-term implications of biomonitoring of foods is being studied by storing about 3 kg of USDIET-I as originally composited. Dietary collections from different regions of the U.S. are currently underway. Representative portions of these total diets from future collections will also be preserved in the Biomonitoring Specimen Bank.

16. Precision in Routine INAA Over a Two Year Period at NBSR

M.J. Blackman (Smithsonian Institution)

Beginning in June 1984 and continuing to date, aliquots of SRM 697 - Brick Clay have been included as a check standard in 61 separate irradiations of archaeological ceramics. The goals of the analysis of the ceramics were to routinely analyze a large number of samples (1100) for as many elements as possible (32 sought) with as much precision as possible. Working within these constraints, irradiations and counting times could not be tailored to specific elements.

The irradiations were carried out with reactor power at 10 mw in the RT-3 pneumatic facility and with reactor power at 20 mw in the RT-1 and RT-4 pneumatic facilities. The length of the irradiations were varied in accordance with the neutron flux in each facility so that the fluence was approximately the same. Samples and standards, in 0.5 mL polyethylene microcentrifuge tubes, were packed in a single band in the "rabbit" to minimize linear flux gradients. No special attention was given to the placement of standards or check standards within the band, and therefore any radial flux variation was not controlled. The gamma counting was carried out on two different detectors with similar resolution, but quite different counting efficiencies (8.3% vs. 34.8%). Two different automated sample changers were used, one with a fixed geometry of 10 cm and the other with variable geometry. Each sample was counted twice, the first count after a 5 day decay and the second after at least a 30 day decay. The counting times were varied according to the detector efficiency and the sample geometry so that the counting statistics were approximately equal for each element determined in each aliquot.

Initially about 10 grams of SRM 679 was dried for 24 hours at 110 °C and cooled and stored in a desiccator. Fifty four nominal 100 mg aliquots were weighed as needed over the two year period, in addition, seven nominal 40 mg. aliquots were also analyzed in separate irradiations. The initial stock of SRM 679 was periodically redried. During this period at least three different balances were used for weighing.

SRM 1633 (coal fly ash) was the comparator standard used to quantify 23 elements in SRM 679. Commercially available computer software was used to process the gamma ray data with several upgrades and a shift in computer systems occurring during the duration of the experiment. In summary, while the requisite care in accordance with good analytical procedures was taken for each analysis, there was a great deal of variability in irradiation facilities, counting equipment, and processing software. The data set for SRM 679 ought then to provide a baseline for analytical precision in instrumental neutron activation analysis over time at a single facility.

The results of 54 analyses of nominal 100 mg samples show that of the 23 elements quantified in SRM 679, over half (14) have a precision of better than 5% (1 standard deviation), with five elements better than 2% precision. Only three elements had precisions worse than 10% Ba-12.9%, Tb-13.0%, and U-15.9%. Typical counting statistics for each of these elements in SRM 679 are: Ba-10.5%; Tb-10.0%; and U-13.3%. For these three elements, all but about 2 to 3% of the sample variance can be attributed to counting error. When the elements with very low counting errors (Sc, Co, La, and Sm) are examined, the sample variance not attributed to counting error is 1 to 1.5%. All random and systematic errors, exclusive of counting error, appear therefore, to contribute only about 1.5% to the sample variance, this includes potential sample inhomogeneity.

The results of the 7 analyses of nominal 40 mg samples are comparable to those for the nominal 100 mg samples. The concentrations for all 23 elements fall within 1 standard deviation in the two sets. The implication is that to within about 1.5% to 2.0%, 40 mg aliquots of SRM 679 and the standard SRM 1633 are both homogeneous and directly comparable to 100 mg. aliquots. Examination of the data sets shows that for a large number of elements instrumental neutron activation analysis can routinely achieve better than 5% precision regardless of changes in irradiation facilities, instrumentation, and computer processing software. With some special effort at tailoring irradiation and counting times to the nuclides displaying less precision, precision of better than 5% could be achieved routinely for all 23 elemental concentrations reported here.

17. Determination of Silicon by Fast Neutron Activation Analysis

D.A. Becker

An instrumental neutron activation analysis method utilizing fast neutrons has been developed for the determination of silicon in a variety of matrices. This method has been applied to the certification of silicon in SRM 1632b, Trace Elements in (Bituminous) Coal, and in the determination of silicon in a number of marine sediments.

The nuclear reaction used for the analysis is the silicon-29(n,p) aluminum-29 reaction, with counting of the 1273 keV gamma-ray (half-life is 6.5 minutes). The sample is irradiated in a boron nitride capsule, which absorbs the thermal neutrons while passing the fast neutrons. This substantially lowers the overall radioactivity of the sample, while not affecting the analytic signal for silicon. In particular, the BN reduces the interference due to production of aluminum-28 by thermal neutrons.

The University of Maryland nuclear reactor was used for the irradiations, since its design (light water cooled and moderated) provides a greater intensity of fast neutrons than the NBS reactor, even though the thermal neutron intensity is less than 3% of the NBSR (which was designed specifically to provide a maximum intensity of thermal neutrons). Irradiation times ranged from one to six minutes, depending on the silicon concentration in the samples.

For the coal analysis, four bottles were analyzed in duplicate, with sample sizes ranging from 0.58 to 0.75 g. The silicon concentration found was 1.35 ± 0.03% (S.D., 1s). Good agreement was obtained between all four bottles.

For the sediment analysis (made as part of a series of specimen bank samples for NOAA and described elsewhere in this report) silicon concentrations ranged from 23 to 31%. Excellent agreement was obtained for check samples of NBS/SRM 1646 (Estuarine sediment), the IAEA sediment samples, and NCR-Canada reference sediments, although none of these are known to a high degree of accuracy.

From the above data, it is estimated that analysis for silicon using aluminum-29 can be made for 2 mg of silicon with approximately 3 percent counting statistics, or 0.2 percent silicon in a one gram sample. Further, if no aluminum or phosphorus is present in the sample, this level could most likely be lowered to 0.02 percent through use of the aluminum-28 isotope. Work is continuing on additional types of samples and to establish experimental detection limits for silicon.

18. Specimen Banking and Analysis in the National Status and Trends Program

R. Zeisler, S.F. Stone, B.J. Koster, and K.D. Diamant

Recently, environmental monitoring has been complemented by programs for systematic and controlled long term storage of environmental samples, i.e., environmental specimen banking (ESB). The necessity, usefulness and importance of ESB has been demonstrated for current monitoring as well as for preserving the representation of the past for examination in future years. In 1984, the National Oceanic and Atmospheric Administration (NOAA) initiated a specimen bank for estuarine and coastal samples as part of its National Status and Trends (NS&T) Program. This specimen bank has been incorporated in the research activities of the Pilot Environmental Specimen Bank which is housed at NBS. The research includes all steps of the ESB operation with special emphasis on quality assurance in the selection, collection, preparation, storage, and analysis of marine samples according to validated procedures.

The NS&T program is sponsoring two monitoring projects for the U.S. coastal waters: the Mussel Watch with 154 collection sites and the Benthic Surveillance with 50 collection sites. The Mussel Watch collects bivalves and sediments from tidal sites whereas the Benthic Surveillance collects bottom feeding fish and sediments from estuarine and continental shelf sites. Over 40 sites nationwide are now included in the ESB. The sampling techniques applied in these programs have been refined and modified in cooperation with the field scientists to fulfill the requirements of the ESB and to ensure comparability between the samples used in real time monitoring and the banked samples. Protocols have been developed for the sampling and preparation of the specimens that greatly reduce the risk of contamination. Special tools and implements, chiefly made from titanium and Teflon, are used to prepare the samples for transport and storage at liquid nitrogen temperature. The samples are prepared for analysis in a clean-room by contamination free blending (sediments) or cryogenic homogenization (tissues) in Teflon disk mills.

A unique sequence of instrumental analytical methods involving x-ray fluorescence and neutron activation analysis procedures has been employed for the determination of 44 elements in marine bivalves. The individual procedures are a x-ray fluorescence method based on backscatter with fundamental parameter corrections, prompt gamma activation analysis, and neutron activation analysis with instrumental and radiochemical procedures. This analytical approach has been expanded to include the analysis of sediments and fish tissues. It is possible to use a single subsample of about 250 mg and follow it through three instrumental analyses, nondestructively, and a final radiochemical procedure, which consumes the sample. The advantage of this approach is obviously the reduced sample preparation which minimizes contamination or loss and assures the true correlation of elements since all results are based on the same subsample, i.e., eliminating uncertainties due to sample to sample variations.

Analytical quality assurance has been accomplished by two means: first, the sequential analytical procedure allows for the independent determination of up to twenty elements by the two or three techniques involved. Since the same subsample is used by all techniques, any deviation of the results would indicate a possible bias of one technique. Secondly, a sufficient number of certified reference materials has been analyzed in parallel with the monitoring samples. Good agreement of the analytical results with the certified values will allow conclusions on the accuracy of the results obtained for the monitoring samples.

Analytical data have been obtained for tissue samples from earlier bivalve specimens and from sediment samples collected during the 1985 NS&T project year. Because of the limited number of individual samples included so far in the ESB, no assessment of the environmental status can be made at this time. However, the primary emphasis of this work on high quality multielement determinations is documented in the results. The implementation of this analytical approach on certified reference materials and control materials designed for the NS&T program was successful.

19. Determination of Total Zinc and Selenium in Human Blood Serum

R.R. Greenberg and G.V. Iyengar (USDA)

Establishment of precise and accurate analytical measurements for trace elements in various biomedical specimens is crucial in order to provide reliable reference values for various applications in environmental and health related investigations. In dealing with biological samples, it is not uncommon to experience contamination or other methodological problems for even such common elements as Cu, Fe, and Zn which occur at relatively high concentration levels in many samples, such as blood serum, milk and urine. Other more analytically difficult elements, e.g., Cr, Mo, Mn, and Se in blood serum, present considerable challenges in obtaining meaningful analytical output. A comprehensive quality assurance (QA) program is an essential requirement for such studies, beginning with the biological and analytical validity of the sampled material, followed by chemical analysis using critically controlled analytical procedures. The requirement for QA is even more important if the analyzed specimen is intended to serve as a reference material. For such uses, it is not only desirable to generate a homogeneous material, but the measurement process applied should be capable of keeping the analytical errors as low as possible, e.g., 1-2%. Such a measurement capability has been demonstrated in our laboratory using instrumental neutron activation analysis (INAA) to determine Zn and Se in a pooled human serum sample.

It is of practical significance to note that real world clinical specimens are very precious, and often they are obtainable only in limited quantities, e.g., blood serum. Therefore, implicit confidence in the chosen analytical technique is necessary. There are many ongoing studies investigating the effects of Zn and Se as protective agents against various types of cancers and nutritional disorders. In view of the ubiquitous nature of Zn, it is often easy to contaminate samples with this element during the sample preparation steps prior to the actual determination step. Selenium is a particularly difficult element to determine in many biological materials in view of the volatility of a number of Se compounds, and the difficulty of decomposing some organo-selenium compounds. In this context, INAA offers a number of advantages compared to other analytical techniques including: high sensitivity; lack of matrix effects; minimal sample pretreatment; and non-destructive capability; which eliminates analytical problems due to sample dissolution and to volatility losses of Se. In addition, the measurements can be repeated on the same samples, if necessary, utilizing the non-destructive nature of the technique.

Zinc and Se have been determined using INAA in seven replicates from a pooled human serum sample provided by the Organic Analytical Research Division. Care was taken in each step of the analysis to keep the total systematic error to one percent or less. Serum samples (approximately 500 mg each) were weighed into acid-washed, ultrapure quartz vials, lyophilized at -40 °C, and sealed. A quartz vial containing 500 μL of high purity (sub-boiling distilled) water was processed simultaneously with the samples as a blank, and two samples of Bovine Liver, SRM 1577 were prepared for use as control samples. A new standard solution was prepared gravimetrically containing both Zn and Se, and was deposited gravimetrically onto filter papers placed inside quartz vials. A Se standard used in the certification analysis of Milk Powder, SRM 1549, was also prepared in the same manner as an additional check. The height of the filter papers in the quartz ampoules was exactly matched to that of the lyophilized serum samples to eliminate both irradiation and counting geometry effects. The samples, standards, controls and blank were irradiated together in two polyethylene irradiation containers (rabbits) for three hours in the RT-3 pneumatic tube facility of the NBS reactor. One month after irradiation, the samples were removed from the rabbits, washed in nitric acid to remove any surface contamination from the quartz vials, and counted at a distance of 5 cm from the gamma-ray detector for approximately one day each. Zinc was quantified using the 1115 keV gamma-ray from Zn-65, and Se quantified using the 136, 265, and 400 keV gamma-rays from Se-75.

The results of this analysis are very encouraging. The observed precision (relative standard deviations) for the concentrations of both elements in the seven replicate samples was one percent, which was consistent with the counting statistics. The Se results obtained using each of the three different gamma-rays were in close agreement, and the observed concentrations in the Bovine Liver control samples were in close agreement with the certified values. The two Se standards agreed to within a few tenths of a percent, and this difference could be explained by the uncertainty due to counting statistics. The concentrations of both elements were in the reference range for "normal" individuals, indicating that this serum pool may be useful as a reference material. It may also be used as a research material for validating methodologies for analytical techniques whose systematic errors are less completely understood than are those of INAA.

In view of the closely bio-regulated concentration levels of many essential elements in tissues and body fluids, it may be necessary to achieve the level of precision and accuracy demonstrated in this investigation, to successfully identify subtle differences, if any, in specimens from normal individuals compared to those from pathological cases.

20. Ion Chromatography Coupled to a Direct Current Plasma for On-Line Matrix Separations

M. Epstein, W. Koch, K. Epler (University of Maryland), and T. O'Haver (University of Maryland)

While the sensitivity of the Direct Current Plasma (DCP) rivals that of the Inductively Coupled Plasma (ICP), the DCP is far more sensitive to sample matrix-induced enhancements or suppressions of emission intensity, which place a finite limit on the accuracy of analytical determinations. Analysis with the DCP requires the use of matrix-matching, electron density buffers, and standard addition to assure the accuracy necessary for the certification of Standard Reference Materials (SRMs). Furthermore, spectral interferences often require a compromise in the choice of analysis parameters, such as the use of a less sensitive emission line or the application of a correction factor, even with the high-resolution echelle spectrometer. Therefore, in certain cases, an on-line separation/preconcentration scheme is needed to obtain a high sample throughput as well as to improve sensitivity and accuracy. Ion chromatography (IC) lends itself well to this application.

We have coupled an ion chromatograph to a wavelength-modulated DCP spectrometer and have investigated its application to the determination of phosphorus in several copper-based Standard Reference Materials. The most sensitive phosphorus line, 213.618 nm, cannot be resolved from the copper 213.598-nm ion line in a copper-based matrix. The phosphorus 253.565-nm line is not affected by copper radiation, but exhibits reduced sensitivity and a severe iron emission line overlap (253.560 nm). The vacuum UV phosphorus lines are not available using the echelle spectrometer. Thus, the determination of phosphorus in copper-based SRMs is difficult without a separation step.

Using an on-line ion chromatographic separation with a cation separator column, we have determined phosphorus in SRM 1251, with a result of 420 ± 40 μg/g, compared to direct DCP analysis using the less sensitive 253.565 nm phosphorus line with a correction factor for the iron interference (440 ± 20 μg/g) and a wet-chemical analysis (392 ± 2 μg/g). Complete chromatographic separation of phosphorous and copper eliminated the phosphorus-copper spectral interference using 50 μL of a solution of the SRM in 10% HCl/HNO_3 at a copper concentration of approximately 2%. However, attempts to improve the sensitivity by using more concentrated solutions of the SRM, up to 10% copper, resulted in overloading of the column and an incomplete separation. Further experiments with a higher capacity column are now underway.

We are also experimenting with the technique of replacement ion chromatography, where the analyte ion is exchanged in a post column with an equivalent number of replacement ions, which are quantified by a detector that is extremely sensitive and specific for the replacement ion. Such a scheme would be an ideal complement for an analytical method such as Laser Enhanced Ionization Spectroscopy, which is extremely sensitive and specific for a limited number of elements.

21. Measurement of ^{9}Be-^{10}Be Isotope Shifts using Doppler-Free Resonance Ionization Mass Spectrometry

J.C. Travis, J. Wen, and J.D. Fassett

The high-resolution resonance ionization mass spectrometry (RIMS) developments reported here are the result of an on-going collaboration with T.B. Lucatorto, C.W. Clark, B.C. Johnson, and R.E. Bonnano of the Radiation Physics Division, Center for Radiation Research. The analytical goal of this effort is to demonstrate isotopically selective laser ionization in order to enhance the ability of conventional mass spectrometers to measure extreme (e.g., 10^{10}) isotope ratios, such as encountered in carbon dating and other geochronological applications. In order to achieve this enhancement, the resonant laser must have a bandwidth much less than the optical isotope shift between the two isotopes to be discriminated, and, in almost all cases, the effects of the Doppler shifts must be drastically reduced.

A laser bandwidth of 150 MHz (0.005 cm^{-1}) at 560 nm has been achieved by substituting a single-longitudinal-mode (< 10 MHz bandwidth) continuous wave dye laser, amplified in 5-ns bursts (at 10 Hz) by a pulsed dye amplifier (PDA), for the normal dye laser head of the second generation RIMS instrument (RIMS II). After frequency doubling the 25 mJ PDA output in an appropriate crystal, 2-3 mJ of light in the region of 280 nm may be obtained. Resonance ionization of Be through high-lying (~70,000 cm^{-1}) energy levels is achieved by uv two-photon excitation followed by photoionization with a more intense (~10 mJ) infrared (1064 nm) laser beam obtained from the Nd:YAG laser used to pump the PDA.

In order to achieve Doppler-free two-photon linewidths, the uv beam is retro-reflected through the mass spectrometer ion source so that the atomic cloud is subjected to counterpropagating beams. In this manner, approximately one-half of the two-photon excitations involve one photon from each of the two beams. For an atom with an arbitrary velocity (speed and direction), this type of excitation cancels the Doppler shift to first order, since the Doppler shifts with respect to the two beams are equal in magnitude and opposite in sign. The remaining two-photon excitation events, involving two photons from the same beam, produce a "pedestal" approximately two orders of magnitude broader and a similar factor lower in amplitude than the Doppler-free peak. The ultimate in analytical performance will require the elimination of this pedestal by means of perfectly circularly polarized laser beams and delta-m selection rules. To date, we have achieved only partial cancellation, but have reasonable expectation of being able to achieve the desired goal.

Doppler-free signals have been used for isotope shift measurements using five Be transitions for a sample with a ^{9}Be:^{10}Be ratio of ~2500:1. For the $1s^2 2s^2$ - $1s^2 2s6s$ $^1S_0$ (71321 cm^{-1}) transition, we have reported an optical isotope shift of 13.31 ± 0.05 GHz, showing a predominant normal mass shift and a small (~2%) specific mass shift. In spite of the demonstrated isotopic ionization selectivity for Be, our "abundance sensitivity," or ability to measure extreme ratios, is limited by the number density of the minor species in the atomic vapor, and by the low duty factor of the pulsed laser system. New atomization methods such as laser ablation and pulsed ion beam sputtering are being explored to improve sensitivity.

22. Ion-Pairing HPLC/AAS for the Determination of Cr(III) and Cr(VI) in Natural Water

A. Syty (Indiana University of Pennsylvania), R.G. Christensen, and T.C. Rains

Although the toxic form of chromium is its +6 oxidation state, current government regulations still limit only the total chromium concentration permissible in natural, drinking, and waste waters. Sensitive measurement of total chromium in aqueous samples is simple and straightforward, but it is obviously desirable to develop reliable, rapid, and sensitive methods for selective determination of the Cr(III) and Cr(VI) species. Such endeavors have recently received some attention in the literature, and papers have been published describing separate determinations of hexavalent and trivalent chromium using solvent extraction, coprecipitation, ion-exchange and chelating resins. Many of these methods are time-consuming, involve a considerable amount of sample manipulation, and are only selective for either one or the other of the forms of chromium.

In previous work, we have experimented with the use of tetrabutylammonium phosphate as a means of on-column preconcentration of Cr(VI). In the present work, we have investigated the ion-pairing reversed-phase HPLC speciation of chromium and improved the method reported in the literature by making it faster and generally applicable to all soluble compounds of Cr(III), as well as Cr(VI). We have also performed a time study of the reduction of Cr(VI) in natural water spiked with Cr(III) and Cr(VI).

Separation of the chromium species was accomplished on a 4-cm long column packed with 5-μm polymeric C_{18} material. The optimum eluent composition proved to be the following: distilled water containing $1x10^{-4}M$ tetrabutylammonium phosphate, $1x10^{-4}M$ ammonium acetate, and sufficient acetic acid to lower the pH to 3.1-3.2. The eluent was pumped through the column at 2.0 mL/min. The column was coupled directly to the capillary of an atomic absorption spectrometer and absorbance was measured at the 357.8-nm Cr line.

A sample of natural water was collected from a pond in mid-March and another sample was collected from the same pond in mid-May when the content of suspended solids was visibly much higher. Five aliquots of each sample were spiked with different levels of Cr(III) and Cr(VI) and sufficient HOAc was added to make the pH = 3.1-3.2. The initial concentrations of Cr(III) and Cr(VI) varied from 0 to 2 μg/mL. Standard Cr(III) and Cr(VI) mixtures containing similar levels of each Cr species were used as comparison standards.

With the eluent composition given above, the elution times are 22 seconds for Cr(III) and 70 seconds for Cr(VI). Since the Cr(VI) peak was slightly broader in the natural water than in the standards, evaluation was done by measuring peak areas. The detection limits were 40 ng/mL for Cr(III) and 80 ng/mL for Cr(VI).

All the spiked samples of pond water showed gradual decreases of Cr(VI) and increase of Cr(III) as a result of reduction by the organic matrix of the natural water. In all cases, the rate of Cr(VI) reduction was higher in the water collected in May than in the water collected in March. For example, it took more than 20 days for 0.4 μg/mL of Cr(VI) to decrease below the detection limit in a sample of water collected in March, but the same level of Cr(VI) in a sample of May pond water took only 5 days to decay below the detection limit.

The average recovery of total chromium added in all the spiked samples of pond water was 101 ± 6%. This outcome supports the validity of the proposed method for Cr(III) and Cr(VI) speciation and measurement in natural waters.

23. Atomic Emission Homogeneity Testing of the New Magnesium Standard Reference Material, SRM 656

J. Norris and T. Vetter

In cooperation with the metals industry, the first of a series of magnesium SRMs has been prepared and tested. The SRM is in the form of a solid disk 51 mm (2 in) in diameter and 8 mm (5/16 in) thick. The surface preparation for analysis by spark optical emission spectrometry is carried out by facing the metal surface on a lathe. The account of material removed is referred to as the surface depth.

No standard ASTM method exists for the spectrometric analysis of magnesium, however, two suggested methods are available. Both suggested methods call for sample excitation using a self-igniting bipolar capacitor discharge in air with a graphite counter electrode. Although this condition could have been implemented on the laboratory spectrometer, a total argon atmosphere with a unipolar capacitor discharge was chosen for the homogeneity test. For test purposes, a 15 s preburn and 20 s exposure period was employed. To determine the within-sample homogeneity, the sample was divided into five pie-shaped pieces, and these plus the center were analyzed multiple times. To determine between-sample homogeneity, seven samples were "grabbed" from the lot of 150 pieces. The spectrometer was calibrated using reference materials originally obtained in 1952 and 1953 from Dow Chemical Co. and Apex Smelting Co.

The results from the within/between seven sample test gave unexpected variation from piece to piece as shown in Table 1 for aluminum.

Table 1. Aluminum SRM 656 Values in %

Piece Number	% Al
1	8.64
2	8.81
3	8.61
4	8.81
5	8.60
6	8.86
7	8.71

Since the pieces had been selected at random and were run in random order, this cyclic variation must have had a special cause. On examination of each sample, it was determined that the samples had been surfaced on different sides with one side having more material removed than the other due to mold marks. Two additional pieces were selected to examine the effects of surface depth on results for aluminum. Successive depths of 1 mm were removed from each piece and an analysis was performed at each depth. The results for this test for aluminum are shown in Table 2.

Table 2. Aluminum SRM 656 Values in %

Analysis Depth (1 mm steps)	Sample 1	Sample 2
1	9.61	9.17
2	8.53	8.37
3	8.06	8.28
4	8.03	8.04
5	7.94	8.06
6	7.98	8.17

The correlation between %Al and depth is evident. When this material is certified, a very careful sampling for chemical analysis will be made and the certified portion specified. For a specified depth from the surface, any portion of that surface may be used for analysis.

24. Real-Time Metal Analysis of Ambient Aerosols

R.L. Watters, Jr., M.S. Epstein, and F. Shen

Air pollution monitoring is presently accomplished by analyzing particulates collected on high-volume air filters. Although this method allows preconcentration of the particulate matter, it has the disadvantage of being a batch process. On-line monitoring of air flows that contain particles is possible by introducing the sample stream directly into an inductively coupled plasma (ICP) or atomic absorption spectrometer (AAS) system.

As part of our material transport studies, we have used the spark discharge as a means of producing fine particles in a stream of argon. Emission spectrometry resulting from ICP excitation of the aerosol allows the direct analysis of conductive metal samples. We have examined the potential of this approach for analyzing particle streams in air by dilution of the argon-borne aerosol with air and introducing the mixture into the ICP. Air entrainment into an ICP usually extinguishes the flame, so a special high-power generator was used to sustain the plasma under various air-flow conditions.

An alternative approach using the air-acetylene flame of an AAS system was found to be a simpler application for air samples. Although the atomic absorption experiment is a single element determination, infusion of the air stream into the flame is more straightforward than into the ICP. Conditions for maximum sensitivity were reached when the sample introduction device was set to provide the entire air flow (10 L/min) for the chemical flame. When ICP excitation is used, less than 1 L/min of air can be tolerated.

Sample aerosol introduction devices that produce a positive air flow can be connected directly to the ICP or AAS. However, to sample ambient air, a device is needed to draw in the aerosol and force it into the plasma or flame region. A small regenerative blower was found to be suitable for ambient air sampling. When coupled to either the ICP or the AAS systems, the blower was used to sample streams of air containing aerosols of Cu, Zn, and Fe. Calibration curves for Fe were linear and the detection limit was less than 0.01 μg/L.

A field test instrument based on the AAS was assembled and taken to a smoke chamber to measure Fe aerosols. Fe was determined at a concentrated smoke condition and at very low levels in the chamber. Consistently linear response was observed for Fe concentrations from 15 μg/L to 0.55 μg/L using different absorption lines of known relative sensitivities. The data were used to predict that the lowest concentration that could be measured with a signal-to-noise ratio of 20 was 0.15 μg/L.

Recent work has focused on the problem of system calibration using aerosol streams of known metal content. A conventional ICP nebulizer system was coupled to a desolvation system to produce dry aerosols in air. The desolvation system consists of a heated tube that evaporates the water droplets, allowing the metal particles to separate in the stream. A cooling condenser follows the heated tube and is used to remove only the water vapor from the air stream. Standard solutions of various metals were nebulized and collected on a filter for a fixed time period. The collected aerosol was then dissolved from the filter and analyzed by conventional ICP spectrometry to ascertain the aerosol generator output. Stable conditions have been established whereby the aerosol delivery rate is reproducible within ±5% relative. Changing the concentration of the nebulized solution changes the concentration of the dry aerosol in a controlled manner. A plot of the measured aerosol delivery rate versus the concentration of the standard solution is linear between 0 and 0.7 μg Fe/L measured aerosol concentration. The standard concentrations used for these measurements ranged from 0 to 1000 μg Fe/mL.

This system will be used to calibrate a new AAS system with the blower connected to the sample inlet. Aerosol transport efficiencies for various particle sizes and geometries will be measured and the effects of static charge on the particles will also be investigated. Measurement capabilities for detecting Pb in automobile exhaust and other metals in smoke from incinerators will be examined.

25. Error Modeling and Confidence Interval Estimation for ICP Calibration Curves

R.L. Watters, Jr., C.H. Spiegelman (NBS), and R.J. Carroll (NBS)

A simple linear calibration function can be used over a wide concentration range for the Inductively Coupled Plasma (ICP) due to its linear response. The random errors over wide concentration ranges are not constant, and constant variance regression should not be used to estimate the calibration function. Weighted regression techniques are appropriate if the proper weights can be obtained. Use of the calibration curve to estimate the concentration of one or more unknown samples is straightforward, but confidence interval estimation for these results is less obvious. We have developed a method for modelling the error along the ICP calibration curve and using the estimated parameters from the fitted model to calculate weights for the calibration curve fit. Multiple and single-use confidence interval estimates are obtained and results along the calibration curve are compared. A particular feature of our approach is that each iteration of the noise model fit is itself a weighted fit using estimates from the previous iteration. We compared a model of standard deviation, Model (1) with a model of variance, Model (2) to estimate calibration variability. The final set of fitted variances is then used for the weighted regression of the straight-line calibration curve. Confidence limits for concentrations obtained using the calibration curve are calculated in a straightforward manner.

We examine the effects of calibration in various ICP analysis schemes in the following example. The measurements were performed on a Perkin-Elmer Plasma II ICP dual spectrometer system using the "A" monochromator. The spectral bandpass of this monochromator is 0.007 nm. The spectral background for Ni at 231.625 nm was measured and subtracted from the peak intensity for each instrumental integration.

A total of nine Ni standard solutions were prepared gravimetrically along with a reagent blank for the zero-standard. The concentrations of the standards ranged from 0 μg/mL to 5.0275 μg/mL. The first analysis of the data included all ten replicates at each of the ten standard concentrations. Since the ICP is often used in laboratories where the sample analysis rate is high, instrumental replicates are limited to as few as four. We therefore examined this case by repeating the fit using only the first four replicates from each set of ten. At this point the data were examined to test the assumption of measurement independence and outliers. The fit of the estimated standard deviation, $\hat{\sigma}(x)$ for the 10 and 4 replicate cases according to model (1) yields parameter estimates with small differences observed between the unweighted case and either of the two weighted fits. These differences have little effect on the remainder of the analysis.

The fit of estimated variance, $\hat{\sigma}^2(x)$, according to model (2) results in the parameter estimates for unweighted, weighted by $1/s^4$, and weighted by $1/\sigma^4$ fitting. The method of weighting has a significant effect on the parameter estimates. The weights, $1/\sigma^2$, for the fit of s using model (1) range over one order of magnitude. However, the weights, $1/\sigma^4$, for the variance fit of model (2) range over two orders of magnitude. Although the high concentration points are important for estimating this fit in the quadratic region, they have extremely low weighting ($1/\sigma^4$). Therefore, the weighted fitting procedure will have difficulty distinguishing between a linear and a quadratic model. Thus, the estimates of the linear and quadratic terms will be poorly determined, although the fit may be quite adequate.

We then examined the fit of the calibration function. Fitting effects on the calibration curve with weights equal to 1.00, $1/s^2$, and $1/\sigma^2_w$ were compared. The coefficient and standard error estimates for the 10-replicate data are quite similar regardless of weighting method. The unweighted case yields slightly different (and erroneous) values for the standard errors. Of course uncertainty interval estimates for an unknown sample concentration cannot be calculated for the unweighted case since homoscedasticity would have to be assumed. No single value for the standard deviation is suitable over the range of calibration.

Using only 4 replicates causes a small change in the slope and a relatively larger change in the intercept, especially for the s^2-weighting case. However, the standard errors for these estimates are large enough to minimize the significance of these differences. In practical applications a more limited range of calibration is appropriate when the chief concern is trace analysis near the intercept. In terms of the standard error of the estimated coefficients, the 4-replicate data represent a minor deterioration in the variability of the fit.

Confidence interval estimation was carried out using $\alpha = 0.10$. It was found that the uncertainty interval for the unknown sample measurement and the calibration uncertainty band contribute almost equally to the total uncertainty. Ignoring either source of variability will result in a significant underestimation of the random error in a sample analysis. Confidence intervals were calculated for 10 and 4-replicate calibration, for single and multiple-use of the calibration curve, and for weighting with $1/\sigma_w^2$ and 1.00 as weights at each x_i. A comparison of single versus multiple use of the calibration curve indicates the expected wider confidence intervals for multiple use.

An important difference in interval width exists between the weighted and unweighted cases. In the latter case, the value of $\sigma_w(x_i)$ is 1.0 and at the low end of the calibration curve, $\hat{\sigma}$ is appreciably larger for the unweighted fit than the weighted fit. The product, $\sigma_w(x_i)\ \hat{\sigma}$, is therefore slightly larger for the unweighted case. This causes an over-estimation of confidence intervals at the low end of the calibration curve.

At the high end of the calibration curve the predicted value for $\sigma_w(x_i)$ for 4 replicates is greater than that for 10, causing the 4-replicate intervals to be wider than the corresponding 10-replicate intervals. At this end of the calibration curve, however, the interval widths for fitting with weights 1.0 significantly underestimate the true interval widths as estimated by the weighted cases. The larger variance at the high end of the calibration curve, as estimated by $\sigma_w(x_i)$ accounts for this difference.

In summary, estimation of the error along the calibration curve is important for weighted regression. Error modelling is more robust than using the standard deviations of the calibration standard measurements themselves, and the iterative weighted fitting procedure is generally applicable. Clearly, if heteroscedasticity is ignored, confidence intervals will be too narrow at the high end and too wide at the low end of the ICP calibration curve.

26. The National Cancer Institute - National Bureau of Standards Round Robin Data Analysis

F.C. Ruegg and R.C. Paule (NBS)

In cooperation with W.E. May and R. Schaffer of the Organic Analytical Research Division and with the National Cancer Institute, round robin interlaboratory studies of α-tocopherol, β-carotene, retinol, selenium and zinc in human serum were performed. A suite of computer programs for data management and reduction were written to analyze and display the data. The following commercial software is used on this project: IBM Basica, Micro Data Base Systems Knowledgeman/2 and Redding Group Graftalk. Knowledgeman/2 is a data base manager which is used to store and manage all of the round robin data. Graftalk is a graphics interpreter which is used for graphics output.

The data for each round robin analysis are entered into an IBM PC-AT computer using the data base manager to allow the data to be edited and manipulated. The data are sorted into the proper order using the data base manager, and a program written in Basica then performs an analysis of variance on the data.

The statistical analysis for each analyte and sample consists of:

1) Calculating a grand mean for each sample and analyte from all reporting laboratories

2) Calculating the standard error of the average of each laboratory's reported result

3) Calculating on both an absolute and relative basis the within and between laboratory components of standard deviation for each analyte

An example of the program output is shown for round robin VII:

```
  Standard Lab                          Analyte=Zinc
Serum   Grand AVG   S.E. AVG   S Within   S Between   % CV AVG   % CV X

 040      0.801      0.018      0.033      0.059        2.2        8.4
 041      1.049      0.020      0.037      0.070        1.9        7.5
 042      1.471      0.026      0.021      0.096        1.8        6.7
 043      1.855      0.037      0.027      0.137        2.0        7.5
 047      0.674      0.027      0.026      0.073        4.0       11.5
 048      1.394      0.048      0.027      0.136        3.5        9.9
```

Using Graftalk, a laboratory's data for a selected analyte in several sera samples can be plotted against the grand means for all reporting laboratories, and a linear least square fit can be calculated and plotted. The data from previous round robins can be combined on the same graph if similar samples have been analyzed in more than one round robin.

Thus far, we have analyzed the data from eight round robins. Each round robin consists of measurements from up to 25 laboratories reporting a pair of replicate measurements on five analytes for up to five different human sera, or on the order of 1200 numbers. This represents approximately 10,000 data points. Each pair of data points requires five ancillary entries to identify uniquely the pair requiring a total of approximately 25,000 computer entries. This approach has proven to be an effective way to evaluate statistical control of a laboratory's analysis of sera for the five analytes of interest.

27. Optical Lifetime Measurements of Laser-Induced Ions in Flames

G.C. Turk and N. Omenetto (Joint Research Center, Ispra Italy)

Laser-enhanced ionization (LEI) spectroscopy utilizes direct electrical detection of element-specific ionization induced as a result of resonant laser photoexcitation. The experiments reported here have combined the ion production aspects of LEI with ion detection by laser induced ionic fluorescence. Although direct electrical detection of laser-induced ionization is certainly more sensitive, the magnitude and temporal profile of the direct signal is very much dependent on the magnitude and uniformity of the electric field, which is typically non-uniform and easily perturbed in a flame. Also, electrical detection is non-specific, whereas fluorescence detection is ion-specific and is not subject to the same types of perturbation as electrical detection. Studies of temporal and spatial profiles of the laser produced ions are straightforward.

Strontium atoms in the air-acetylene flame are directly photoionized in two steps provided by one dye laser tuned to the resonance ground state transition (460.733 nm) and by the excimer pump beam at 308 nm, partially split from the amplifier section of the dye laser. The ions produced are then monitored by a third laser beam, collinear and counterpropagating in the flame, tuned to an ionic fluorescence transition and variably delayed with respect to the ionizing beams.

With the ionizing laser off, the fluorescence probe laser excites only the Sr^+ ions that are present in the flame as a result of unassisted thermal ionization of the aspirated Sr. A natural thermal ionization fraction of 12% was measured for Sr at 10 μg/mL by observing the increase in the resonance atomic fluorescence of Sr at 460.733 nm, which occurs when the thermal ionization is suppressed by the addition of 1000 μg/mL of Cs. Under the same conditions, the magnitude of the laser-produced Sr^+ ionic fluorescence was found to be 1.8 times that of the natural level, for a laser ionization yield of 25%. For comparison, an ionization yield of 14% was estimated from the integrated current in the direct electrical signal pulse, the estimated laser/atomic interaction volume, and the estimated Sr atomic number density in the flame.

The time history of laser-produced ions showed two distinctly different decay modes. An exponential decay of 58 ns time constant consumes 85% of the laser produced ions before equilibrium is reached. The remaining 15% decay takes place with an exponential time constant of 57 microseconds. The slow decay is in a time range consistent with ion-electron recombination and with the physical transport effects of diffusion and flame gas flow. Cs excesses of 10-, 30-, and 100-fold decreased the slow decay component to 14.8, 7.2, and 2.9 microseconds, respectively. This behavior is consistent with expected recombination behavior in the presence of the excess electrons provided by Cs.

The fast decay process is unaffected by the presence of Cs buffer and is too fast to be related to any physical transport. However, changes in the fast decay behavior with fuel-to-oxidant ratio suggest that the fast decay is the result of chemical reaction of Sr^+ with flame constituents. In the theoretical models of the LEI process, which have been developed using rate equation analysis, the only ion loss mechanism considered has been that of recombination. The possibility of a very fast chemical reaction loss has never been considered, and further study will be necessary to evaluate the consequences of such fast decay.

28. Standard Reference Materials

B.I. Diamondstone

This year has been the first full year during which the Division has implemented the concept of "Technical Champions". This involves the use of selected senior staff to interact with the project manager from the Office of Standard Reference Materials (OSRM) to provide technical oversight for the entire process of producing a Standard Reference Material (SRM). The two major projects that have been implemented under this program are the preparation of a replacement Trace Elements in River Sediment SRM and the preparation of a new Trace Elements in Bovine Serum SRM. Both projects are in process and the interaction between Division 551 and OSRM has been quite satisfactory. Hopefully, this new concept will gain full acceptance and will prove to be an excellent way to establish a direct link between the analysts and the project managers. To date, more than one dozen Technical Champions have been identified and are at various stages in producing new standards.

During this year, considerable emphasis has been placed on important areas of the SRM certification process. Attempts have been made to provide estimates that are more accurate, both for the amount of time required to carry out analyses and the cost of these analyses. Much discussion has revolved around the use of preliminary analyses to identify potential problem areas that could be encountered during the actual certification process. This has triggered a search for rapid, inexpensive, multi-element techniques which would be used to avoid pitfalls which can delay predetermined deadlines and lead to expensive cost overruns. In addition, considerable effort has been expended in the area of identifying and resolving biases between techniques.

As in the past, there are three sources of support for work on SRMs: Scientific and Technical Research Services funds (STRS) provided by OSRM are intended for the preliminary research necessary to develop the methodologies required for the actual production of SRMs; Working Capital Funds (WCF) are intended for the actual production of SRMs and; STRS funding from the Technical Division is often used to resolve unforeseen analytical problems which occur during the certification process. The relative amounts of funding from the above mentioned sources are presently in the ratio of approximately 1:4:2. Input to all SRM projects is provided by the entire scientific staff and most often involves cooperative work by staff from all Groups in the Division.

Listed below are different areas of research that were funded by OSRM during the past year.

STRS Projects Supported by OSRM during FY86

Task	Description
Phosphorus in Steels	Research to eliminate the matrix effects and to develop selective separation procedures for the determination of 1-100 μg of P. Research is in progress.
Silicon in Fuels	Research leading to the development of an improved nuclear method for the determination of Si in fossil fuels. Preliminary measurements have been made and initial results indicate that analyses can be carried out for samples containing 0.2% Si in a one gram sample.
SRM Analysis by RIMS	Research leading to the determination of Cr, V, Ti, and Mo in SRMs by RIMS. Work is in progress to develop processing procedures and to develop the systematics of the multielement experiment.
ICP-Mass Spectrometry	Continued research leading to the application of Inductively Coupled Plasma Mass Spectrometry to the analysis of SRMs. Tin and lead have been determined in Monel with no preconcentration.
pH Buffers	Research leading to improved accuracy of pH standardization. Work is in progress on long term stability of electrodes and on the determination of the ion size parameter.
Electrolytic Conductance	Research leading to the determination of absolute electrolytic conductance standards. Work is in progress to replace existing Organisation Internationale de Metrologie Légale (OIML) standards with the new NBS standards.

Once again, analyses were carried out on more than 60 different SRMs covering a wide variety of matrices including metals, fossil fuels, foods, glasses and environmental materials. 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:

Selected Standard Reference Materials Analyzed During FY86

SRM Number	Title
2670	Freeze Dried Urine
2677	Be/As on Filters
88b	Dolomitic Limestone
1549	Powdered Milk
97b	Flint Clay
98b	Plastic Clay
2689-2691	Fly Ashes
1638b	Reference Fuel
1616-1617	Kerosene
1641b-1642b	Trace Elements in Water
1575	Pine Needles
1572	Citrus Leaves
1567a	Rice Flour
1568a	Wheat Flour
931c	Liquid Absorbance Filters
1634b	Fuel Oil
679	Brick Clay
1632b	Coal
1577	Bovine Liver
2423	Ductile Iron
C1248	Monel
2695	Fluoride in Vegetation
1244b-1247b	Inconel and Incoloy
332	Copper Concentrate
2100's	Spectrometric Solutions
120c	Phosphate Rock
2694	Simulated Rainwater
1260-1265	Low Alloy Steels
2676c	Trace Metals on Filters
1930	Extended Range Filters
1621c-1622c	Residual Fuel Oils
2678,2680,2681	Blank Filters

As in the past, a number of elements were determined this year in some SRMs for which these elements were not certified in past years. These additional analyses are part of a program to continually update existing SRM certificates in response to requests from customers. In addition, material preparation is underway this year for the replacement Oyster Tissue SRM and the Fluoride in Vegetation SRM, as well as a series of seven new Low Alloy Steel SRMs.

Among the new SRMs being worked on during the past year are the Extended Range Filters, River Sediment, Low Alloy Steels, Leads, and Trace Metals in Blank Filters.

C. Outputs and Interactions (Inorganic Analytical Research Division)

1. Publications

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Zeisler, R., "Foreword: Symposium on Standardization of Collection and Preparation of Biomedical Samples for Trace Element Analysis," NBS J. Res., 91, 45-56 (1986).

Zeisler, R., "The Sampling and Analysis of Human Livers," NBS J. Res., 91, 75-85 (1986).

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Zhang, Y. Z., Watters, R. L., Jr., and Rains, T. C., "Determination of Phosphorus in Refractory Materials by Inductively Coupled Plasma Atomic Emission Spectrometry," Submitted for publication.

Zielinski, W. L., Jr., Hughes, E. E., Barnes, I. L., Elkins, J. W., and Rook, H. L., High Accuracy Standard and Reference Methodology for Carbon Dioxide in Air, U. S. Department of Energy, DOE/PR-06010-31, TR033, 1986.

2. Talks

Epstein, M. S., Turk, G. C., and Travis, J. C., "Evaluation of ND^1-YAG and Copper-Vapor Pumped Dye Lasers as Excitation Sources for Atomic Fluorescence Spectrometry," 12th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, October 2, 1985. Invited.

Travis, J. C., Fassett, J. D., and Moore, L. J., "Thermal Vaporization Resonance Ionization Mass Spectrometry," 1985 Annual Meeting of the Optical Society of America, Washington, D.C., October 17, 1985. Invited.

Gramlich, J. W., "The Determination of the Atomic Weights of the Elements at NBS," Department of Chemistry, George Washington University, Washington, D.C., October 25, 1985.

Rains, T. C., "The Art of Sample Preparation for Spectrochemical Analysis," "Determination of Trace Elements in Refractory Materials by Atomic Absorption and Emission Spectrometry," "Applications of Electrothermal Atomization Atomic Absorption Spectrometry," and "Research and Development in Atomic Spectrometry," Shanghai Institute of Ceramics, Shanghai, China, October 25-31, 1985. Invited.

Walker, R. J. and Moore, L. J., "Resonance Ionization Mass Spectrometry (RIMS) for the Measurement of Multi-Element and Re-Os Isotopes in Crystal Rocks," 96th Annual Meeting of the Geological Society of America, Orlando, FL, October 30, 1985.

Rains, T. C., "Trace Elemental Analysis in Environmental Samples by AAS," Shanghai Institute of Testing Technology, Shanghai, China, November 1, 1985. Invited.

Rains, T. C., "The Art of Sample Preparation" and "Research and Development in Atomic Spectroscopy at NBS," Institute of Geochemistry, Guiyang, China, November 3-5, 1985. Invited.

Kelly, W. R., "The Determination of Sulfur and Uranium by Thermal Ionization Mass Spectrometry," Department of Chemistry, University of Missouri-Rolla, November 4, 1985. Invited.

Travis, J. C., "Resonance Ionization Mass Spectrometry for Trace Metal Analysis," Department of Chemistry, University of Michigan, Ann Arbor, MI, November 5, 1985. Invited.

Rains, T. C., "Characterization of Standard Reference Materials by Atomic Absorption and Inductively Coupled Plasma Atomic Emission Spectrometry," and "The Art of Sample Preparation," Institute of Geochemistry, Guilin, China, November 8-9, 1985. Invited.

Rains, T. C., "Characterization of Standard Reference Materials by Atomic Absorption Spectroscopy," Institute of Environmental Chemistry, Beijing, China, November 11, 1985. Invited.

Rains, T. C., "The Art of Sample Preparation," Research Institute for Atomic Energy, Beijing, China, November 12, 1985. Invited.

Rains, T. C., "Characterization of Standard Reference Materials by Atomic Spectroscopy," Research Institute for Standard Materials, Beijing, China, November 13, 1985. Invited.

Rains, T. C., "Trace Elemental Analysis in Ores, Minerals and Metals by AAS," General Research Institute of Mining and Metallurgy; Beijing, China, November 16, 1985. Invited.

Rains, T. C., "Research and Development in Atomic Spectroscopy at NBS," Spectroscopy Society of China, Xang Shan Hotel, Xang Shan, China, November 17, 1985, Plenary Lecture.

Rains, T. C., "Characterization of Standard Reference Materials by Atomic Absorption and Inductively Coupled Plasma Atomic Emission Spectrometry," 1st Beijing Conference and Exhibition on Instrumental Analysis, Beijing, China, November 18, 1985, Plenary Lecture.

Travis, J. C., Fassett, J. D., and Moore, L. J., "Resonance Ionization Mass Spectrometry, First International Laser Science Conference, Dallas, TX, November 20, 1985. Invited.

Rains, T. C., "Trace Elemental Analysis in Non-Ferrous Metals by Atomic Spectroscopy," General Research Institute for Non-Ferrous Metals, Beijing, China, November 21, 1985. Invited.

Rains, T. C., "Determination of Trace Elements in Fossil Fuels by AAS," 1st Beijing Conference and Exhibition on Instrumental Analysis, Beijing, China, November 21, 1985.

Whelan, David P., "Square-Ware Voltammetry at Microelectrodes," November 27, 1986.

Zeisler, R., "The Role of Specimen Banking in the NOAA Status and Trends Program," NOAA/NBS Quality Assurance Workshop, National Bureau of Standards, Gaithersburg, MD, December 5-6, 1985. Invited.

Zeisler, R., "Protocols for Sampling," NOAA/NBS Quality Assurance Workshop, National Bureau of Standards, Gaithersburg, MD, December 5-6, 1985. Invited.

Iyengar, G. V., "Biological Trace Element Research: Recent Developments," Department of Chemistry, University of Kentucky, Lexington, KY, December 13, 1985. Invited.

Kingston, H. M., "Understanding the Acid Coupling in Microwave Dissolution," CEM Corporation, Charlotte, NC, December 14, 1985.

Fleming, R. F., "Analytical Applications of Neutrons," Workshop on an Advanced Steady State Neutron Facility, National Bureau of Standards, Gaithersburg, MD, December 16, 1985.

Carpenter, B. S., "Science as a Career," Junior Science and Humanities Symposium, Georgetown University, Washington, D.C., January 9, 1986. Invited.

Greenberg, R. R., "Preparation of High Quality Multielemental Standards for Instrumental Neutron Activation Analysis," ASTM Task Group on Nuclear Methods of Chemical Analysis (E10.05.02), New Orleans, LA, January 14, 1986. Invited.

Bowman, R. C., Jr. and Downing, R. G., "Boron Implantation Behavior Through SiO_2 Film on $Hg_{0.7}Cd_{0.3}Te$," American Physical Society, Atlanta, GA, January 27, 1986.

Kingston, H. M., "Laboratory Robotics," Society for Applied Spectroscopy, Gaithersburg, MD, January 28, 1985.

Barnes, I. L., "The Atomic Weights of the Elements - 1985. An Analysis of Uncertainties," Inorganic Analytical Research Division Seminar, February 11, 1986.

Fleming, R. F., "Analytical Applications of Neutrons," Seminar, Department of Chemistry, Indiana University of Pennsylvania, Indiana, PA, February 17, 1986.

Iyengar, G. V., "Trace Element Analytical Chemistry in Medicine and Biology," India Institute of Science, Bangalore, India, February 21, 1986. Invited.

Kingston, H. M., "The Certification of Vanadium in Human Serum at the ppb Level using IDMS," Indiana university of Pennsylvania," Indiana, PA, February 21, 1986.

Iyengar, G. V., "Trace Elements in Relation to Public Health Problems," Bhabha Atomic Research Center, Bombay, India, February 27, 1986. Invited.

Marinenko, G., "Potential Reference Methods for Free Alkali and Alkaline Earth-Ions," AACC Ionized Calcium Symposium, Galveston, TX, February 27, 1986. Invited.

Iyengar G. V., "Multielement Analyses of Biological and Dietary Reference Materials: An Update of the Current Status," Central Department for Chemical Analyses, Nuclear Research Center, Jülich, FRG, March 3, 1986. Invited.

Fassett, J. D., "Analytical Systems-RIMS," NBS Staff Research Seminar, March 4, 1986.

Paulsen, P. J., "Application of ICP-MS to Isotope Dilution Analysis of Standard Reference Materials," ICP-MS Symposium, Pittsburgh Conference, Atlantic City, NJ, March 10, 1986. Invited.

Riley, J. E. and Downing, R. G., "Quantitative Depth Profiling of Boron in Glass with Neutrons," Pittsburgh Conference, Atlantic City, NJ, March 13, 1986.

Fleming, R. F., "Analytical Applications of Neutrons," Seminar Department of Nuclear Engineering, University of Michigan, Ann Arbor, MI, March 14, 1986.

Marinenko, G., "Development of Methods for Sodium Ion Activity Measurements in Biological Fluids," National Meeting of the National Committee for Clinical Laboratory Standards, Baltimore, MD, March 20, 1986. Invited.

Downing, R. G., "Neutron Depth profiling of Technologically Important Materials," State University of New York, Buffalo, NY, March 21, 1986. Invited.

Epstein, M. S., Velapoldi, R. A., Blackburn, D. A., and Picciole, G. L., "Evaluation of Uranyl-doped Glass Microspheres as Standards for Fluorescence Immunoassay," 86th Annual Meeting of the American Society for Microbiology, Washington D. C., March 26, 1986.

Kingston, H. M., "The Use of Microwave Energy in Acid Decomposition of Samples for Trace Elemental Analysis," SOHIO, Cleveland, OH, March 26, 1986.

Iyengar, G. V., "Accurate Measurements of Trace Elements in Biological Tissues," Rutgers University, Department of Chemistry, New Brunswick, April 1, 1986. Invited.

Koch, W. F. and Liggett, W. S., "Critical Assessment of Detection Limits for Ion Chromatography," ACS National Meeting, New York, NY, April 15, 1986. Invited.

Rains, T. C., "State of the Art of Atomic Absorption Spectrometry," 5th NBS-ADBASE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, April 15, 1986.

Iyengar, G. V., Tanner, J. T., Wolf, W. R., and Zeisler, R., "Preparation and Characterization of Mixed Diet Composite USDIET-I: Determination of Energy, Phytic Acid and Elemental Concentrations," Working Paper presented at the IAEA Research Coordination Meeting on Coordinated Research Programme on Human Daily Dietary Intakes of Nutritionally Important Trace Elements, Vienna, April 15-18, 1986.

Zeisler, R., "Incorporation of the Total Diet Concept in the U.S. Biomonitoring Specimen Bank," IAEA Research Coordination Meeting, Vienna, Austria, April 15-18, 1986. Invited.

Epstein, M. S., "Comparison of Detection Limits in Spectroscopic Methods of Analysis," 191st National Meeting of the American Chemical Society, New York, NY, April 16, 1986. Invited.

Gramlich, J. W., "Inorganic Mass Spectrometry Applications," The 1986 NBS Analytical Chemistry/Materials Science Workshop, Nat. Bur. Stds., Gaithersburg, MD, April 17, 1986. Invited.

Kelly, W. R., "Chemical Separations," 5th NBS-ADBASE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, April 17, 1986. Invited.

Barnes, I. L., "Inorganic Mass Spectrometry," The 1986 NBS Analytical Chemistry /Materials Science Workshop, Nat. Bur. Stands., Gaithersburg, Md., April 17, 1986. Invited.

Zeisler, R. and Iyengar, G. V., "Specimen Banking of Foods for Biomonitoring of Inorganic Constituents," International Workshop Trace Element Analytical Chemistry in Medicine and Biology, Neuherberg, F. R. Germany, April 21-23, 1986.

Rains, T. C., "Preparation of Environmental Samples for Trace Metal Analysis," EPA/Kansas City Section of SAS, Kansas City, MO, April 24, 1986, Keynote Address.

Zeisler, R., Iyengar, G. V., Tanner, J. T., Wolf, W. R., "Preparation and Analysis of Nutritional Materials for Quality Assurance," Second International Symposium on Biological Reference Materials, Neuherberg, F. R. Germany, April 24-25, 1986. Invited.

Lucatorto, T. B., Travis, J. C., Fassett, J. D., and Clark, C. W., "High Resolution Laser Techniques in Resonance Ionization Mass Spectrometry," Department of Energy Contractors Workshop on Advanced Laser Techniques for Chemical Measurements, Seattle, WA, April 29, 1986. Invited.

Wen, J., Johnson, B. C., Travis, J. C., Fassett, J. D., Bonanno, R. E., and Lucatorto, T. B., "Determination of the $2s^2\text{-}6s^1S^9\text{Be-}^{11}\text{OBe}$ Isotope Shift via Resonance Ionization Mass Spectrometry," American Physical Society, Washington D. C., April 29, 1986.

Kelly, W. R., "Detection of COMOS-1402 in the Stratosphere," Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada, May 8, 1986. Invited.

Carpenter, B. S., "Nuclear Chemistry and its Applications," Seneca Valley High School, Germantown, MD, May 15, 1986. Invited.

Iyengar, G. V., "Trace Metals in the Diet and in Biological Specimens," National Institutes of Health, National Cancer Institute, Bethesda, MD, May 16, 1986. Invited.

Epstein, M. S., Diamondstone, B. I., Hilpert, L. R., Miller, M. M., Chesler, S. N., and Gills, T. E., "Progress in the Development of a New River Sediment Reference Material, Symposium on Chemical and Biological Characterization of Municipal Sludges, Sediments, Dredge Spoils and Drilling Muds," Cincinnati, OH, May 20, 1986.

Epstein, M. S., "The Certification and Use of Standard Reference Materials from an Analyst's Viewpoint," Cincinnati, OH, May 20, 1986. Invited.

Walker, R. J., Fassett, J. D., and Shirey, S. B., "The Use of Resonance Ionization Mass Spectrometry for Examining the Re-Os Isotopic Systematics of Archean Komatities," Geological Society of America Ann. Conf., Baltimore, MD, May 22, 1986.

Iyengar, G. V., "Selenium and Zinc in Human Serum from Different Global Regions," Second NBS/NCI Micronutrient Analysis Workshop, Gaithersburg, MD, May 28, 1986. Invited.

Greenberg, R. R., "Determination of Zinc and Selenium in Human Blood-Serum by Neutron Activation Analysis," Second NBS/NCI Micronutrient Analysis QA Workshop, Gaithersburg, MD, May 28, 1986. Invited.

Turk, G. C., "New Developments in Laser Enhanced Ionization Spectroscopy," Department of Physics Colloquium, Chalmers University, Goteborg, Sweden, May 29, 1986. Invited.

Zeisler, R., "Recent Developments in Analytical Methodology Related to the U.S. Specimen Bank Program," Colloquium, Institute for Applied Physical Chemistry, Nuclear Research (KFA), Jülich, F. R. Germany, June 2, 1986. Invited.

Lindstrom, R. M., "Cold-Neutron Prompt-Gamma Activation Analysis at ELLA: Recent Measurements," Institute for Applied Physical Chemistry, Kernforschungsanlage Jülich, Germany, June 2, 1986.

Wen, J., Johnson, B. C., Travis, J. C., Lucatorto, T. B., and Clark, C. W., "Measurement of ^{9}Be - ^{10}Be Isotope Shifts by Doppler-free Resonance Ionization Mass Spectrometry," Gordon Research Conference on Multiphoton Processes (Poster Session), New London, NH, June 9, 1986.

Johnson, B. C., Wen, J., Travis, J. C., Fassett, J. D., Bonanno, R. E., and Lucatorto, T. B., "Determination of the $2s^2 1S$-$6s\ ^1S\ ^9$Be-^{10}Be Isotope Shift via Resonance Ionization Mass Spectrometry," 17th Annual Meeting of the Division of Electron and Atomic Physics, American Physical Society, Eugene, OR, June 18, 1986.

Zeisler, R., "Multielement Studies on Total Diets and Human Materials Including Analytical Quality Control," Seminar on Multielement Studies, Nuclear Research Center (KFA), Jülich, F. R. Germany, June 19, 1986. Invited.

Greenberg, R. R., "Multielement Neutron Activation Analysis - A Valuable Tool for Environmental Studies," Seminar on Multielemental Studies, KFA, Jülich, FRG, June 19, 1986. Invited.

Lindstrom, R. M., "Determination of Environmental I-127 and I-129 by Neutron Activation," Department of Radioecology, Swedish University of Agricultural Sciences, Uppsala, Sweden, June 19, 1986.

Kelly, W. R., "Determination of Picogram Quantities of Uranium by Thermal Ionization Mass Spectrometry," ASTM Seminar: Alpha Particles and Semiconductors, National Bureau of Standards, June 19, 1986.

Downing, R. G., "Analysis of Optical Signal Processing Materials by Neutron Depth Profiling," International Meeting on Nuclear Analytical Methods, Orleans, France, June 20, 1986.

Stone, S. F., Hancock, D., and Zeisler, R., "Characterization of Biological Macromolecules by Electrophoresis and Neutron Activation," Modern Trends in Activation Analysis, Copenhagen, Denmark, June 23, 1986.

Downing, R. G., Maki, J. T., and Fleming, R. F., "Analytical Applications of Neutron Depth Profiling," 1986 Modern Trends in Activation Analysis, Copenhagen, Denmark, June 23, 1986.

Zeisler, R. and Young, I., "The Determination of Chromium-50 in Human Blood and Its Utilization for Blood Volume Measurements," 7th International Conference Modern Trends in Activation Analysis, Copenhagen, Denmark, June 23-27, 1986.

Iyengar, G. V., "Sample Validity in Biological Trace Element Research Studies," Modern Trends in Activation Analysis, Copenhagen, June 23-27, 1986. Invited.

Barnes, I. L., "Inorganic Mass Spectrometry," Center for Analytical Chemistry Summer Seminar, Nat. Bur. Stands., Gaithersburg, MD, June 23, 1986. Invited.

Watters, R. L., Jr., Epstein, M. S., Rains, T. C., and Comeford, J. J., "Real-time Analysis of Metal Aerosols," 1986 Chemical Research and Development Conference, Department of the Army, Edgewood, MD, June 24, 1986. Invited.

Lindstrom, R. M., "Activation Analysis Opportunities using Cold Neutron Beams," 7th International Conference on Modern Trends in Activation Analysis Conference, Copenhagen, June 25, 1986.

Stroube, W. B. and Lutz, G. J., "Analysis of Foods for Iodine by Epithermal Neutron Activation Analysis," 7th Modern Trends in Activation Analysis Conference, Copenhagen, June 25, 1986.

Becker, D. A., "Primary Standards in Activation Analysis," 7th International Conference on Modern Trends in Activation Analysis, Copenhagen, June 26, 1986.

Fleming, R. F. and Lindstrom, R. M., "Precise Determination of Aluminum by Instrumental Neutron Activation Analysis," 7th International Conference on Modern Trends in Activation Analysis, Copenhagen, Denmark, June 26, 1986.

Greenberg, R. R., "The Role of Neutron Activation Analysis in the Certification of NBS Standard Reference Materials," 7th Int'l Conf. on Modern Trends in Activation Analysis, Copenhagen, Denmark, June 27, 1986. Invited.

Iyengar, G. V., "International Studies on Dietary Intake of Trace Elements by Human Subjects," Nuclear Research Center, Jülich, June 30, 1986. Invited.

Greenberg, R. R., "Elemental Characterization of the NBS Milk Powder Standard Reference Material via Instrumental and Radiochemical Neutron Activation Analysis," University of Pavia, Pavia, Italy, July 1, 1986. Invited.

Iyengar, G. V., "State of the Art of Trace Element Analysis Techniques and Reference Values for Elemental Concentrations in Human Tissues and Body Fluids," Reference Man Task Group Meeting, International Commission on Radiological Protection, Oak Ridge, Tennessee, July 9, 1986.

Iyengar, G. V., "Dietary Intakes of Minor and Trace Elements by Human Infants and Adults: A Global View Based on Some Recent International Studies," Reference Man Task Group Meeting, International Commission on Radiological Protection, Oak Ridge, Tennessee, July 10, 1986.

Koch, W. F., "Standard Reference Materials for Acid Deposition Measurements," 1986 Johnson Conference, Johnson, VT, July 17, 1986. Invited.

Beary, E. S., "Isotope Dilution Mass Spectrometric Assay of Copper in Copper Ore Reference Materials," SAC 86/3rd BNASS University of Bristol, Bristol, England, July 24, 1986.

Greenberg, R. R. and Fleming, R. F., "High Accuracy Analysis of Biological Materials by Neutron Activation Analysis," Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, MD, September 3, 1986. Invited.

Fassett, J. D. and Walker, R. J., "Ultratrace Elemental and Isotopic Analysis of Osmium and Rhenium Using Resonance Ionization Mass Spectrometry and Thermal Vaporization," 3rd International Resonance Ionization Spectroscopy Symposium, Swansea, Wales, September 9, 1986.

Travis, J. C., Fassett, J. D., and Lucatorto, T. B., "Resonance Ionization Mass Spectrometry," 3rd International Resonance Ionization Spectroscopy Symposium, Swansea, Wales, September 9, 1986.

Pratt, K. W., "High Accuracy Differential Pulse Arodic Stripping Voltammetry Using Indium as an Internal Standard," ACS National Meeting, Anaheim, CA, September 11, 1986.

Mavrodineanu, R., "Chemical Calibration Standards for Molecular Absorption in Spectrometry," Conference on Advances in Standards and Methodology in UV-Visible-NIR Spectrometry, Oxford, England, September 16, 1986. Invited.

Watters, R. L., Jr., "ICP Calibration over Wide Concentration Ranges," FACSS 13, St. Louis, MO, September 29, 1986. Invited.

Walker, R. J., and Fassett, J. D., "Ultratrace Elemental and Isotopic Analysis of Osmium and Rhenium Using Resonance Ionization Mass Spectrometry (RIMS) and Thermal Vaporization," 13th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, MO, September 29, 1986.

Epler, K., Epstein, M. S., Koch, W. F., O'Haver, T. C., "Improving the Accuracy and Sensitivity of Atomic Spectroscopic Methods Using Ion Chromatography," 13th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, MO, September 30, 1986.

Watters, R. L., Jr., Epstein, M. S., Harnly, J. M., and Miller-Ihli, N., "Real-time Analysis of Ambient Aerosols," FACSS 13, St. Louis, MO, October 3, 1987.

3. Committee Assigments

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

Donald A. Becker

Member, 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
- ASTM D-19.33, Water Associated with Synthetic Fuel Production

Chairman, ASTM E-10.05.12, Task Group on Nuclear Methods of Chemical Analysis

Member, ANS, Trace Element Analysis Committee, Technical Group on Biology and Medicine

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

Stephen B. Carpenter

Member, Institute of Nuclear Materials Management, Standards Committee N15.9.3, Non-destructive Assay (Physical Methods)

Technical Consultant, U.S. House of Representatives, Committee on Science and Technology, Science Policy Task Force

Commissioner and Member of the Board of Directors, Commission on Professionals in Science and Technology

Member, American Nuclear Society, International Committee and the Isotopes and Radiation Division, Nuclear and Atomic Analysis Technical Committee

Finance and Housing Chairman and member of Technical Committee, International Conference on Methods and Applications of Radioanalytical Chemistry, Kona, Hawaii, April 5-10, 1987.

Council, Joint Board on Science and Engineering Education

Member, National Bureau of Standards, Radiation Safety Review Subcommittee

Robert G. Downing

Member, ASTM E-10, Nuclear Methods for Chemical Analysis

Member, Inorganic Analytical Research Division Seminar Committee

Chairman, Inorganic Analytical Research Division Safety Committee

Michael S. Epstein

Member, ASTM D-19, Water

Treasurer, Society for Applied Spectroscopy

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

John W. Gramlich
Member, Institute of Nuclear Materials Management, Committee N15.9.3, Non-Destructive Assay (Physical Methods)
Member, International Union of Pure and Applied Chemistry, Commission on Atomic Weights and Isotopic Abundances

Robert R. Greenberg
Member, ASTM E-10.05, Nuclear Radiation Metrology
Member, NBS Chemistry Storeroom Committee
Member, ANS, Trace Analysis Committee, Technical Group for Biology and Medicine

Govindaraja V. Iyengar
International Commission on Radiological Protection, Task Group on Reference Man
International Union of Pure and Applied Chemistry, Subcommittee on Selenium
International Scientific Committee of the Modern Trends in Activation Analysis
Vice-President, International Union of Elementologists (India)
Member, Editorial Board, the Science of the Total Environment (U.K.)
Advisor, Food Laboratory Newsletter (Sweden)

Howard M. Kingston
Member, ASTM C-26.05, Methods of Test
ASTM C-26.07, Waste Materials
Session Chairman and Eastern Analytical Symposium
Technical Consultant, Congressional Science and Technology Committee

William F. Koch
Member, 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
Chairman, ASTM D-22.03, Task Group on pH
ASTM D-22.06, Atmospheric Deposition
Personnel Officer, NBS Child Care Association, Board of Directors
Member, National Committee for Clinical Laboratory Standards

John K. Langland
Chairman, NBS Electronics Storeroom Committee

Richard M. Lindstrom
Alternate Member, NBS Reactor Safety Evaluation Committee

George Marinenko
- Member, ASTM D-19, Water
- Chairman, D-19.05.04.03, Voltammetry
  - D-19.09.06, Redox Potentials in Saline Water
  - D-19.09.07, pH in Saline Water and Brines
  - D-19.09.01, Chlorine Residuals in Saline Water
- Chairman, National Capital Section of the Electrochemical Society

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
- Secretary/Treasurer, National Capital Section of the Electrochemical Society
- Member, NBS Inorganic Analytical Research Division Safety Committee
- Member, Inorganic Analytical Research Division Seminar Committee
- Member, Research Information Subject Specialist

Theodore C. Rains
- Member, 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
- 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
- Post-Chairman, FACSS Governing Board
- Professor-in-Charge, ACS Short Course on Atomic Absorption and Plasma Emission Spectroscopy
- Task Force Leader, Scientific Instrumentation Information Network and Curricula (SIINC) for Project on "Atomic Absorption Spectroscopy"
- Column Editor, Journal of Applied Spectroscopy

Thomas W. Vetter

- Member, ASTM E-02, Emission Spectroscopy
  - ASTM E-02.02, Statistics
  - ASTM E-02.04, Sampling and Standards
  - ASTM E-02.06, Lead, Tin, Zinc
  - ASTM E-02.07, Aluminum
  - ASTM E-02.09, Ferrous
  - ASTM E-03, Chemical Analysis of Metals
  - ASTM E-03.01, Ferrous
  - ASTM E-03.91, Editorial
  - ASTM E-03.92, Standards
- Chairman ASTM E-03.01, Task Group on Low Concentration of Sulfur in Cast Iron, Combustion Method

Yung-Chi Wu

- Member, ASTM D-19, Water
- Member, NBS/NML Minority Advisory Panel

Rolf L. Zeisler

- Member, NBSR Safety Evaluation Committee
- Chairman, Trace Element Analysis Committee, Technical Group for Biology and Medicine, American Nuclear Society

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 employs 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 the following functional lines: Bioanalytical Techniques, Electrochemistry, Gas Chromatography, Liquid Chromatography, and Mass Spectrometry. Current activities in each of the groups will be discussed in the Group Overviews and Technical Reports that follow. The Division responds to the measurement and standards needs of industry, other government agencies, (Federal, state, and local) public and private institutions and associations, and other research organizations at the National Bureau of Standards. Research efforts in the Division during the past year have resulted in the publication of 25 articles in archival journals and other technical media. An additional 22 articles are currently in press. Division scientists also presented 38 talks at technical meetings and conferences during FY86.

During the past year, approximately 45 percent of our efforts were directed toward basic research in organic analytical chemistry. The remainder of our efforts were in support of other Federal Agency programs and to a limited degree in short-term projects performed on a service analysis basis. The Division is actively involved in four Competence Building Programs that have been selected for funding by the NBS Director. Three of these programs, Organic Electrochemistry, Analysis of Ionization Mechanisms and Ion Structures in Organic Mass Spectrometry, and the Use of Proteins in Analytical Chemistry have been on-going for several years. Accomplishments in all of these areas will be discussed in the Group Overviews and Technical Reports. During the past year, some very exciting research has begun on the development of Bioanalytical Sensors. The objective of this new Competence Building Program is to combine the selectivity inherent in immunological recognition with chemistry-based procedures for signal amplification to provide highly specific and ultra-sensitive chemical sensors. Additional details concerning this research are found in the Bioanalytical Techniques and Electrochemistry Group overviews and Technical Report 6. Research on liquid chromatographic retention mechanisms and high field NMR have also continued with base support.

As in the past few years, the major portion of our other agency support has come from the National Cancer Institute (NCI) and the Environmental Protection Agency (EPA), with substantial support also being provided by the Department of Energy (DoE), Department of Defense (DoD), Department of Agriculture (USDA), and the National Oceanic and Atmospheric Administration (NOAA). Specific research efforts in support of these other Federal agency programs included: serving as Reference Laboratory and Analytical Quality Assurance Center for a network of NCI supported laboratories investigating the efficacy of selected vitamins and other organic micronutrients as cancer chemopreventive agents; continuing to develop reference materials and providing analyses of EPA audit and quality control samples as part of the process for establishing NBS traceability; developing analytical procedures for the determination of polar PAH derivatives and providing reference compounds and characterized complex mixtures for DoE laboratories involved in the investigation of health effects associated with exposure to complex environmental mixtures; continuing the development of an isotope dilution gas chromatography/mass spectrometry method for determining human exposure to chemical warfare agent BZ for the DoD; collaborating with the Center for Radiation Research in the development of an analytical method for performing post-irradiation dosimetry on meats for the USDA; and providing methods development and specimen banking support for the EPA and for NOAA's National Status and Trends monitoring program. Information concerning these activities are provided in the Group Overviews and Technical Reports.

Several short-term projects were also undertaken on a service analysis basis in support of several NBS and other Federal Agency programs. A few examples follow that indicate the wide variety of measurement problems that we are asked to address with rapid turnaround: a method for analysis of fugitive emissions from a paper shredder-burner device was developed for the Navy and utilized on several samples; an apparatus was constructed, a method developed and several samples analyzed to determine methylene bromide leakage from batteries in artillery proximity fuses in a DoD supported project for Harry Diamond Laboratories; several metal surfaces were analyzed for the Naval Research Laboratory to determine if hydrocarbon films were present that might explain the loss of paint adhesion on the surfaces; and the identity of a tear gas neutralizer was determined using fast ion bombardment mass spectrometry and high field NMR. In addition, PCB levels were determined in transformer fluids of transformers taken from the White House.

The collaborative research efforts that were begun several years ago with the other two Divisions in the Center for Analytical Chemistry have continued. The research effort with the Gas and Particulate Science Division for development of an isotope dilution GC/MS method for verifying the concentrations of volatile toxic organics in air SRM cylinders is nearly completed and is described in Technical Report 20. Laser ionization mass spectrometric and Raman spectroscopic measurements are continuing to be performed to assist in determining structures of chromatographic supports for biomolecule affinity chromatography. Our efforts with the Inorganic Analytical Research Division involving neutron activation analysis of two-dimensional electrophoretic slab gels to study protein-metal binding interactions are still on-going and we have provided our expertise in HPLC in the development of methods for the determination of metallo-organic chelates in water. Collaborative research efforts are also on-going with several other technical Centers within NBS. Details concerning our collaborative efforts with the Centers for Chemical Physics, Fire Research, Radiation Research, and the Institute for Materials Science and Engineering are found in the Group Overviews and Technical Reports.

We have continued our active support of the NBS Standard Reference Materials Program. SRM related activities represented approximately 10% of our budget. Measurements for the certification of eleven SRMs have been completed during FY86 and measurements are currently in progress on an additional five materials. Analyses were performed to monitor the stability of an additional six SRMs. Details concerning many of these activities will follow in various Group Overviews. The development of SRMs for drugs of abuse in urine, marine sediment (with certified values for PAH, chlorinated pesticides and PCBs), fat-soluble vitamins in human serum, and molecular weight markers for electrophoresis are among the dozen projects that we will undertake in FY87. Development and certification of the marine sediment SRM will be funded by NOAA and development of fat-soluble vitamins in serum material will be supported by

NCI. All other SRM related activities will be supported solely by the NBS Office of Standard Reference Materials.

Research efforts in the Division have been bolstered by the contributions of approximately 20 research associate and guest workers during the past year. Research efforts in our Gas Chromatography, Electrochemistry, and Bioanalytical Techniques Groups were strengthened by NRC Postdoctoral Research Associates, Howard Mayfield, Damian Shea, and Michael Ambrose, respectively. Dr. Polly Ellerbe, a Research Associate supported by the College of American Pathologists, continues to make significant contributions in our Definitive Methods in Clinical Chemistry Program. Three foreign Visiting Scientists, Dr. Emil Schonberger (National Physical Laboratory of Israel), Dr. S. D. Yang (Chinese Academy of Medical Science in Beijing), and Professor Zeng-nan Zhou (East China Institute of Textile Science in Shanghai) have made major contributions in several Other Agency measurement programs. Dr. P. V. Sundaram (Max Planck Institute in Berlin) has provided us with guidance in the area of enzyme immobilization and stabilization. Professor Barry K. Lavine (Clarkson University) is utilizing his expertise in multivariant analysis to assist scientists in our Bioanalytical Techniques and Liquid Chromatography Groups. The addition of Dr. Anne L. Plant, a biochemist assigned to our Bioanalytical Techniques Group, and Laurie L. Brown, a biomedical engineer working in our Electrochemistry Group, to our full-time staff has provided additional strength, enthusiasm and a number of innovative ideas in our Bioanalytical Sensors research program.

In FY87 we will continue to direct a substantial portion of our efforts in each of the Division's five groups towards basic research. Details concerning these activities are found in the three-year research plans found in the individual Group Overviews. We will also continue to advocate the utilization of our measurement expertise, gained in part from these basic studies, along with our quality assurance experience and background to fulfill Reference Laboratory functions in long-term national monitoring programs. We are currently fulfilling such a function for the NCI Cancer Chemoprevention Program, the DoE Health Effects from Exposure to Complex Mixtures Project, and the NOAA National Status and Trends Program. During the coming year, we anticipate commencing a Reference Laboratory/Quality Assurance function for the EPA Integrated Air Cancer Project and the EPA component of the NHANES-III Program.

The three-year research plans that are included in the individual Group Overviews include equipment needs necessary to completely fulfill those plans. Our general purpose equipment allocation for FY87 will be utilized to purchase a triple quadrupole mass spectrometer and a capillary supercritical fluid chromatograph. Other vital pieces of equipment will be acquired with Other Agency support. Our foremost personnel need is for a protein chemist to help support our biotechnology program. Other pressing needs are for a separations chemist with experience in nutritional measurements to support our NCI efforts and a mass spectrometrist to assist in the development of drugs of abuse in urine SRMs.

1. Bioanalytical Techniques Group: Overview

The activities of the Bioanalytical Techniques Group are primarily directed towards (1) developing means for separating and characterizing proteins, peptides, and other biomolecules for standards needs in biotechnology, (2) synthesizing organic compounds labeled with stable isotopes for high accuracy work in clinical/nutritional chemistry, (3) maintaining expertise and performance of research in high-field nuclear magnetic resonance spectroscopy, and (4) investigation of the use of immunochemical reactions to provide selectivity for the fluorimetric detection of biomolecules.

During the past year we have continued to make progress on the research goals set forth in the Bioanalytical Competence Program. The focus of research with proteins and peptides has been to develop ultra-sensitive methods for protein separation, visualization, and identification. During the characterization phase of this work, specific applications have been attempted to demonstrate state-of-the art capabilities for protein separations. Such work includes studies of viral proteins, honey proteins, effects of reagents on electrophoresis, and use of new materials for chromatographic separations.

Viral protein studies have attempted to identify new proteins produced in the membranes of cells grown in tissue culture and infected with viruses such as the respiratory syncytial virus (RSV). This work has been done in collaboration with the Uniformed Services University of the Health Sciences. We are currently awaiting the installation of an imaging system that will allow matching of proteins from different two-dimensional electrophoretic gels. This new tool should help identify subtle protein differences in infected cells that have been collected at selected time intervals during the viral infection phase.

Studies of the proteins isolated from honey have led to the interesting observation that the isoelectric focusing patterns have encoded in them information which allows differentiation based on their geographical origin. The results from this investigation are being submitted for publication in ELECTROPHORESIS (see Technical Report 5).

Studies of protein separations are continuing with the synthesis of new immobilized polyvinylpyrrolidone (PVP)-metal-redox matrices. The action of immobilized PVP-copper oxidants such as periodate, persulfate or permanganate is being tested on human serum proteins. Different oxidants may have affinity for or react with specific groups of proteins present in the serum. Similarly, the action of immobilized reducing agents (e.g., $SO_3^=$, $S_2O_4^=$, BH_4^-, etc.) on proteins will be examined. The synthesis of hexadecyl modified silica is being investigated for protein immobilization.

Our studies of the effects of reagent purity on electrophoretic separations continue to focus on sodium dodecyl sulfate (SDS). Electrophoretic separations of the same protein can vary depending upon the source of SDS. Many SDS samples were analyzed for chain length, for pH in aqueous solutions, for conductivity, and for spectral properties. In addition, HPLC analyses were performed on solutions of the SDS samples utilizing a C_{18} column with conductivity detection. Analysis for the presence of free alcohols in the SDS samples was also achieved by quantitative derivatization. Critical micelle concentrations of several of the SDS samples were established by a spectroscopic dye method. Currently, electrophoretic separations of selected proteins are being performed using the different SDS samples to correlate the analytical data.

As part of the advancement of a refined isotope-dilution mass-spectrometric definitive method for measuring uric acid in serum (with uric acid-$\underline{1},\underline{3}$-$^{15}\underline{N}_2$ as the internal standard), optimal conditions were developed for isolating uric acid from serum constituents using ion-exchange chromatography and for derivatization by silylation to a stable product for analysis by

GC/MS. This work, done in conjunction with the Mass Spectrometry Group is described in Technical Report 15.

Using the upgraded Bruker WM-400 NMR spectrometer, we have studied the ring conformations of a group of fortimicin aminoglycoside antibiotics by proton NMR spectroscopy at high field. This work is directed towards correlating the ^{15}N NMR chemical shifts with chemical conformations. In 2-D NMR spectrum-editing studies, a new Pascal compiler has been used to speed computations by a factor of 4-5, and phase-sensitive 2-D NMR spectrum editing has been investigated further. In work designed to characterize solid sugars used in measurements of enthalpy of combustion, the utility of high-field proton NMR of dimethylsulfoxide solutions for analysis of the anomeric composition of these sugars has been confirmed by parallel studies using cross-polarization--magic angle spinning ^{13}C NMR to analyze the solid sugars directly.

Eight ^{15}N-enriched aminodeoxy monosaccharides are being synthesized. These sugars will be used as model compounds for ^{15}N NMR investigation of the relationship between ^{15}N NMR spectral parameters, i.e., chemical shift and ^{15}N-^{1}H coupling constants, and molecular structure. Currently, several partially protected sugars are being prepared in conjunction with an investigation to determine optimum reaction conditions for the synthesis.

Feasibility studies on probing the mechanism of a protein silver stain by ^{109}Ag NMR have been completed. Ammoniacal silver solutions with various water soluble amino acids were studied to determine if it would be possible to identify silver binding sites. The shifts observed with methionine and histidine indicated that binding occurs but that the systems also undergo exchange reactions. Low temperature work (-40 °C) failed to give resolution of the broadened ^{109}Ag signal. It was concluded that the experimental and interpretational problems were sufficiently complex that work has been terminated.

We are continuing to work on developing capabilities for enzyme and other protein immobilization by solid-phase binding with the newer "spacer-arm" techniques. For example, urease was immobilized on a variety of different polymeric supports by different coupling mechanisms. The retained enzyme activity of columns packed with immobilized enzyme varies from support to support and also varies with the coupling technique used. At present there are 8 columns that have been studied for nearly one year. Five columns have retained between 76% to 87% of their activities. This work also has application to our recently initiated biosensor development program.

We have also been active in coordinating a national interlaboratory comparison study to assign activity values to the enzyme aspartate aminotransferase (ASAT) in connection with our clinical chemistry standards program. A reference material with accurately assigned activity measurements will soon be issued.

As part of a National Cancer Institute project, and as a prelude to development of a fat soluble vitamin calibration solution SRM, ethanolic solutions for retinol, tocopherol, and beta-carotene have been prepared. For the ethanolic standards, each vitamin solution will be produced with and without the addition of butylated hydroxytoluene (BHT). These solutions will be stored at -25 °C, -80 °C, and liquid nitrogen temperatures. The stability of these standards will be followed during the coming year by spectroscopic and by HPLC analysis to facilitate the detection of possible oxidation products. We have also prepared a series of serum pools which have been sent to participating laboratories. Statistical reporting of the results is proceeding.

During the past year, a NRC/NBS Postdoctoral Research Associate (M. Ambrose) has begun work in the synthesis of labelled sugars to correlate chemical shifts with changes in structure. Dr. A. Plant also joined the group to provide expertise in liposome technology as well as in immunology and enzymology. A post-doctoral candidate is being sought to work in the area of chemically-modified proteins and protein separations with emphasis on enzyme immobilization and stabilization, or on protein/peptide structure and function. A permanent staff member is being sought to develop an in-depth program in studying protein stabilization and in studying chemical interactions between proteins and other biomolecules, including polymers and other supports. Spectroscopic studies including fluorescence studies of protein folding will be included.

Future directions for the Bioanalytical Techniques Group include the development of better techniques for protein/peptide separation and detection. We will continue to extend our capabilities to immobilize enzymes on solid supports and monitor enzymatic activity. We will continue our work on organic synthesis of stable isotopes for high-accuracy clinical and nutritional studies. Research in high-field NMR spectroscopy will be directed towards developing optimal pulse sequences for NMR studies of peptide and other biomolecule structures. Research on biosensor development will include investigation of newer methods of immobilizing enzymes for specific applications in biosensor methodology and the development of immunological and enzymatic approaches to liposome sensitization and lysis.

Dennis J. Reeder, Group Leader; Lyle A. Alexander, Michael G. Ambrose, Alex Cohen, Bruce Coxon, Jesse J. Edwards, Alex J. Fatiadi, Joyce F. Graf, Diane K. Hancock, Ken Keiler, Margaret C. Kline, Millard Maienthal, Kristy L. Richie, Robert Schaffer, P. V. Sundaram, Paul Vetter.

2. Electrochemistry Group: Overview

During the past year the electrochemistry group has focused its efforts on three principal areas of research: (1) development of methods for selective electrochemical detection in liquid chromatography, (2) study of the chemistry and physics of electrode surface modification with polymer-immobilized catalysts, and (3) investigation of the use of immunochemical reactions to provide selectivity for the electrochemical determination of bio-molecules. The common goal of this work has been to increase the sensitivity and selectivity of voltammetric measurements. The research tools we have used to achieve this goal include: square-wave, differential pulse, and cyclic voltammetry; chronoamperometry and chronocoulometry; rotating ring-disk voltammetry; as well as hybrid techniques such as spectroelectrochemistry and liquid chromatography with ultraviolet/visible absorbance (LCUV) and electrochemical (LCEC) detection.

We have continued to make progress on the research goals targeted in the Electrochemistry Competence Building Program. Polymer-modified electrodes have been constructed for the reduction of ethylene dibromide and the selective concentration of anionic analytes at the electrode surface. Extending the original research of Professor Allen Bard of the University of Texas, we have developed a stable, polymer-modified reference electrode for use in nonaqueous media. This device received one of the prestigious I-R 100 awards for 1986. Considerable progress has been made in addressing programmatic needs in NBS/Other Agency programs by the application of LCEC/UV to the determination of fat-soluble vitamins in human serum, nitro-polynuclear aromatic hydrocarbons in air and diesel particulate extracts, and phenylalanine/tyrosine radiolytic products as part of the effort to develop an analytical method for post-irradiation dosimetry on meats.

In collaboration with the Bioanalytical Techniques Group, work has begun on the development of electrochemical and optical sensors for the trace determination of organic analytes. The goal of this project is to use the specificity of immunological recognition coupled to chemical amplification to provide highly selective and sensitive detection. One step toward this goal is the encapsulation of an electroactive marker in the aqueous volume trapped in a lipid vesicle (liposome). Amplification of an immunological binding event may then be achieved by the lysis of the liposome, releasing thousands of marker molecules for subsequent detection. We are currently developing a flow-injection system with the immunochemical reaction taking place on the surface a packed column. The antibody is covalently bound to small glass beads and a solution of antigen-liposome/marker complex mixed with the unknown solution is used to competitively bind to the immobilized antibody. Unbound antigen-liposome/marker complex is carried downstream for non-selective detergent lysis, providing a chemically amplified signal proportional to the unknown antigen concentration. A voltammetric or fluorometric flow-cell detector completes the measurement process. The entire flow-injection system is under computer control, with separate solution and timing sequences for the entire process: generation/regeneration of the reactor column, competitive binding of the analyte/liposome solution, lysis of the unbound liposomes, and detection of the released markers.

One important accomplishment, which is both an outgrowth of the effort in chemically modified electrodes and in the development of biosensors, has been the development of an electrode that selectively preconcentrates anionic marker compounds for subsequent square-wave voltammetric detection. The electrode is based on an oxidized platinum surface derivatized with a trichlorosilylethylpyridine reagent. The covalently-bound pyridine group is easily quaternized with methyl iodide. This creates an anion exchange polymer at the surface of the platinum. The electrode may be used to preconcentrate the ferrocyanide marker released by lysis of liposomes either in the heterogenous flow reactor system or in a homogeneous assay. The advantages of the new electrode are that the electrochemical current measured at the modified surface is about two orders of magnitude larger than at the bare platinum, and the modified electrode dces not exhibit the fouling problems observed at bare electrodes in the presence of serum samples.

In addition to the development of polymer materials for the modification of electrodes, we have also made progress in the mathematical description of the response obtained at these electrodes. For the common situation, where the rate of charge transport through the film on the electrode is slow, we have developed a model with finite-element digital simulation of the various charge transport rate-limiting parameters. As an experimental model system, we have studied the electrochemistry of ferrocene in polyethylene oxide electrolyte. This solid/viscous liquid reveals - in extreme - the effects of uncompensated resistance and slow diffusion of the analyte. From the results of cyclic voltammetry as a function of temperature, an activation energy for diffusion was calculated to be 5 kcal/mol. From the diffusion-controlled portion of a chronoamperometric measurements, the diffusion coefficients could be calculated at various temperatures. Again, an activation energy of 5 kcal/mol was found. This experimental system has provided many new insights into the behavior of polymer-modified electrodes.

An important aspect of the Group's efforts using LCEC/UV has been in the support of two Other Agency projects, the determination of retinol, tocopherol, and carotene in serum as part of our Reference Laboratory function for the National Cancer Institute (NCI) Cancer Chemoprevention Program and the measurement of radiolytic products of phenylalanine and tyrosine, as part of a study for the United States Department of Agriculture (USDA), aimed at developing methods for post-irradiation dosimetry in meats. State-of-the-art chromatographic separations as well as selective detection methods have been developed and utilized to support these projects. In addition, a new approach for the determination of 1-nitropyrene in diesel particulate extracts has been developed, using a solid-phase extraction column to fractionate the sample before determination by reductive, amperometric LCEC.

During the past year we have been assisted by the efforts of several temporary staff members. A NRC/NBS Postdoctoral Research Associate (D. Shea) has begun work on the determination of organic and inorganic sulfur compounds in marine sediments using LCEC. During part of the summer of '86 a general physical scientist (S. Ehlers) assisted in this work. From 3/85 to 6/86, we benefited from the assistance of a guest scientist from the National Physical Laboratory of Israel (E. Schonberger), who supported our efforts in the LCEC of vitamins in serum. During the past year, we have also benefited from the work of a guest scientist from the Chinese Academy of Medical Sciences in Beijing (S. D. Yang), who has contributed to the effort in the LCEC of radiolytic products and the determination of nitro-PAH. We have increased our efforts in the area of the development of biosensors by the recruitment of a biomedical-engineer (L. Brown) and a biochemist (A. Plant, who is assigned to the Bioanalytical Techniques Group).

During the past year we acquired a UV/visible spectrophotometer, a phase-resolved fluorescence spectrometer, and three computers (2 IBM PC-AT for mathematical modeling and an Apple IIe for the control of the flow injection system) for use in our biosensors program. To support the vitamins in serum work, a wavelength programmable LC absorbance detector and an autosampler were purchased.

In the coming year, in addition to continuing or completing our current projects, several new areas of work will begin. In the area of LCEC, a new project on the determination of organotin compounds in marine sediments will begin. This work will "dovetail" nicely with both the OSRM goal of developing a natural marine sediment SRM and our current research on organothiols in sediments. Also, we would like to begin research on ultra-micro and array electrodes for use in both liquid and supercritical fluid chromatography.

In the research on charge transport in polyethylene oxide, we would like to extend our models to the cyclic voltammetric response of these systems. Goals in the modification of electrode surfaces include: controlled synthesis of polymer layers to thicknesses of only hundreds of angstroms, which should allow faster permeation of the analyte and not exhibit the large, uncompensated resistance problems of the thicker films studied to date; research silane reagents that may be used with copolymers for coupling to the surface of the electrode.

Future directions for the biosensors project include the design and development of practical devices and systems for the detection of hormones, drugs, and vitamins in urine and blood.

William A. MacCrehan, Acting Group Leader; Elmo A. Blubaugh, Laurie L. Brown, Sharon Ehlers, Rosanne M. Kannuck, Emil Schonberger, Damian Shea, Shu De Yang, and William T. Yap.

3. Gas Chromatography Group: Overview

The Gas Chromatography Group conducts research in the areas of high resolution gas chromatography, advanced sample preparation techniques and computer automation to allow the development of new techniques and maintain state-of-the-art measurement capabilities, which are used to certify complex Standard Reference Materials (SRMs), address the measurement needs of Other Agencies and disseminate technical information.

The Laboratory Information Management System (LIMS), which was initially structured in FY85, continues to grow in size and utility. Additional software was developed allowing users more latitude in data manipulation. In particular, a program was written allowing manual integration and digital smoothing under cursor control. This program allows us to make corrections to peaks improperly integrated by software-driven data acquisition computers. Additional software allows the transfer and manipulation of both graphical and numeric data between any of the computers within or remotely connected to the LIMS system.

Our efforts in supercritical fluid capillary chromatography (SFCC) have not proceeded for lack of adequate instrumentation. However, during the past year a modest effort has resulted in the construction of a supercritical CO_2 extraction apparatus for rapid and efficient removal of trace organic species from solid samples. This apparatus has been shown to be able to extract PAHs from SRM 1649 (Urban Particulate Matter) and PCBs from sediment in less than 1 hour with efficiencies equal to a 16-hour Soxhlet extraction. This work has also resulted in an archival publication.

The program on the theoretical optimization of the multidimensional gas chromatographic experiment has been successfully concluded and a second manuscript has been prepared for publication. Our postdoctoral appointee, Howard T. Mayfield, upon the completion of 18 months at NBS has left to accept a position with the Department of Defense. Additional work needs to be done to apply the theoretical models of the sequentially coupled column experiment to complex separations.

A gas chromatograph with a mass selective detector (MSD) has been acquired and installed. This instrument gives the Group the ability to make extremely selective analyses at the 10-100 pg/g level. It also allows us to utilize the isotope dilution method of internal standardization. If desired, this detector can also yield mass spectral data for qualitative analysis. To date, the MSD has been used for the quantitation of minor PAH constituents in air particulate samples, the certification of pesticides and PCBs in SRM 1588 (Cod Liver Oil), the isotope dilution measurements of ng/g levels of volatile organics in CRM cylinders, and the qualitative analysis of the constituents in the exhaust of a document shredder-burner. Software has been written to allow information from the MSD data system to be transferred to the LIMS system.

As in past years, the Group has directed a great deal of its efforts to the solution of Other Agency measurement problems. Under a new agreement with the National Oceanographic and Atmospheric Administration (NOAA) we have developed written sample collection and analytical procedures for the determination of PAH, pesticides and PCBs in marine sediment and bivalves. We have also analyzed a number of sediment and tissue samples as part of a "Specimen Banking" component of our Reference Laboratory function of NOAA's Mussel Watch and Benthic Surveillance Program. In our efforts to produce a marine sediment SRM, we are developing a tributyl tin analysis protocol. Thirty new human-liver samples, from the NBS/EPA Environmental Specimen Bank, were analyzed for pesticides and PCB congeners using a recently modified, sample preparation procedure (see Technical Report 22). Three sets of Quality Assurance Materials from EPA/Cincinnati were analyzed and NBS traceability established. Three PCBs on Terrestrial Sediment materials have been homogenized and analyzed, also for EPA/Cincinnati, to be used in their Quality Assurance Program. The Group also prepared and analyzed three alcohol in iso-octane quality assurance materials for EPA Research Triangle Park (RTP). Funding from EPA/RTP has enabled the GC/MS isotope dilution method to be refined for measuring parts-per-billion high-pressure gas standards. Procedures for preparation, storage and analysis of a volatile hydrocarbons in whole blood quality assurance materials are being developed for EPA/Las Vegas.

The Group has made a modest contribution to the Division's SRM program. Three separate alcohol in reference fuel SRMs were prepared and certified this year. These SRMs, 1837-39, contain various alcohols commonly added to gasolines and will be of use to the petroleum industry as well as Federal, state, and local regulatory agencies. Measurements of the Cod Liver Oil Research Material (RM 1588) have been repeated using the MSD equipped gas chromatograph and the material now has certified values and has been re-released as an SRM. PAH content in the GC Performance/Coal Tar SRM is being determined at the present time.

Additionally, the Group has performed a number of service analyses for other Governmental Agencies. We have determined the PCB concentration of transformer fluids taken from the White House, the rate of leakage of methylene bromide from fuse batteries for the Harry Diamond Laboratories, the chemical composition of the exhaust from a document burner for the Department of Defense, and latent hydrocarbon residue analysis for the Naval Research Laboratories.

While the Group is heavily committed to its Other Agency and SRM work, we realize the need to concurrently pursue an active research program in order 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 attain proficiency in multidimensional gas chromatography and would like to attract a Postdoctoral Research Associate in this area. This technique will be increasingly needed for the separation of moderately polar solutes in extremely complex matrices such as nutrients and flavors in foodstuffs and heteroatom polycyclic aromatic compounds (PAC) in environmental particulate materials. We are eager to expand into the area of supercritical fluid capillary chromatography. With SFC instrumentation we will be able to broaden our spectrum of analytical capability to include bio-molecules, vitamins and nutrients, and thermally fragile molecules such as non-chlorinated pesticides and drugs of abuse. We will also investigate the use of the new capillary column technological breakthroughs, ultra-thin films and high temperature phases and columns, for new areas of application such as the high resolution separation of di- and triglycerides. Finally, we want to develop new analytical methods for certification of needed SRMs such as tributyl tin in a marine sediment matrix.

Stephen N. Chesler, Group Leader; Franklin R. Guenther, Reenie M. Parris, Lauren E. Perry, Richard E. Rebbert, Michelle M. Schantz, and Michael R. Summers.

4. Liquid Chromatography Group: Overview

The activities of the Liquid Chromatography Group continue to be focussed on (1) gaining a better understanding of the mechanisms of retention and selectivity in liquid chromatography (LC), and (2) applying this information to the development of methods for the isolation, separation, identification, and quantification of individual components in various mixtures and natural 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. Investigations of the use of small-angle neutron scattering (SANS) for the physical characterization of alkyl bonded phases are continuing. Using SANS, the pore network of porous silica and controlled pore glass has been shown to be fully accessible to chromatographic solvents even after alkyl surface modification. Initial SANS experiments to determine the thickness of the alkyl layer have shown that the resolution of the technique is sufficient to distinguish between C_8 and C_{18} monolayers (see Technical Report 17). Work in progress will use SANS to investigate the orientation of the alkyl chains (i.e., extended vs. collapsed) on the substrate surface as the polarity of the mobile phase changes.

Investigations of selectivity in reversed-phase LC have been directed towards the comparison of selectivity on a variety of alkyl phases with particular emphasis on the comparison of monomeric and polymeric alkyl phases. Polymeric C_{18} phases have been shown to provide greater selectivity for the separation of polycyclic aromatic hydrocarbons (PAH) than monomeric phases and separation of PAH isomers is related to the shape of the solute. In the past year, these studies have included preparation and characterization of (1) C_{18} phases prepared with dichloro and trichlorosilanes, (2) long-chain alkyl phases such as C_{30}, and (3) novel alkyl phases with potentially more rigid chains than conventional phases. These studies are directed towards the development of a "model" of the physical nature of alkyl bonded phases, e.g., the thickness and the surface density of the alkyl layer, the extent of cross-linking in polymeric alkyl phase prepared with multifunctional silanes, and the orientation of the alkyl chains.

The LC Group is heavily involved in the application of LC to the measurement of trace-level analytes in various samples as part of the NBS Standard Reference Materials Program and in support of projects for Other Federal Agencies including the Environmental Protection Agency (EPA), Department of Energy (DoE), National Cancer Institute (NCI), Department of Agriculture (USDA), and National Oceanic and Atmospheric Administration (NOAA). Specific SRM activities are discussed in the Division overview.

We have collaborated with the Inorganic Analytical Research Division (551) in the development of LC methods for the separation of metal chelates and the combination of LC methods with atomic absorption spectrometric (AAS) detection.

Ion-pairing LC has been used for preconcentration and determination of Cr(VI) in the presence of Cr(III) using AAS detection. We are also assisting the Inorganic Analytical Research Division in the preparation of a C_{18} modified silica substrate with three concentration levels of carbon for use as an SRM for carbon determination. The development of this SRM is a direct result of a joint effort with Division 551 during the past several years to determine carbon content in LC packing materials. In conjunction with the GC Group, research in the use of supercritical fluid extraction for the isolation of analytes of interest from various matrices is in progress. Development and validation of this extraction technique will provide a valuable alternative to conventional extraction procedures which will be useful in a number of our projects, particularly in SRM certification, where two independent methods for sample preparation as well as analyses are desired.

During the past year, we have been funded by the Office of Standard Reference Materials to investigate the feasibility of developing an SRM for the characterization of LC columns. An extensive literature survey has been conducted and discussions held with a number of researchers to determine the types of solutes used by various laboratories to evaluate such column properties as carbon loading, selectivity, phase type, residual silanols, etc. Based on the results of the literature survey and discussions, test mixtures of selected solutes will be prepared and used to evaluate the properties of a number of reversed-phase LC columns. Based on these results, a suitable column performance SRM will be developed.

During the coming year, several new SRMs will involve LC measurements including: fat-soluble vitamins in serum, a re-issue of SRM 1647 (PAH in solvent), and a drugs of abuse (THC and metabolites) in urine material. A major new effort will be directed towards the certification of a marine sediment SRM for various organic pollutants.

In support of the NCI Cancer Chemoprevention Project, we have used LC methods and differential scanning calorimetry to determine the purity of commercial vitamin standards; investigated approaches for the measurement of ascorbic acid in serum; evaluated the use of supercritical fluid extraction to remove vitamins from serum; determined the relative absorptivities of β-carotene in various solvents; investigated the feasibility of using direct-injection techniques for the determination of vitamins in human serum, and established protocols for the banking of serum samples in the specimen bank facility.

A new project sponsored by EPA's Integrated Air Cancer Project involves the standardization of an LC fractionation scheme for the isolation of mutagenic components in air particulate samples. Initially, we will investigate the LC retention behavior of selected "marker" compounds which will be representative of various fractions, e.g., PAH, nitro-PAH, aza-arenes, quinones, phenols, etc. Based on these retention data, specific compounds will be selected to serve as markers to standardize the collection of fractions for further chemical and biological characterization.

We made extensive LC measurements on three samples (an air particulate extract, a diesel particulate extract, and a diesel particulate sample) for the determination of PAH and nitro-PAH as part of an international round robin study sponsored in part by the Coordinating Research Council and DoE (see Technical Report 25). These LC measurements, in conjunction with the GC/MS and LC/EC results, will serve as benchmark values for the study in evaluating the data from the various laboratories. As a result of this study, we have extensive information on the comparison of LC and GC/MS methods for the determination of these compounds in complex environmental samples.

The LC Group has also been involved in several Other Agency projects such as the determination of herbicides in a water sample to provide NBS traceability for an EPA QA material, the development of LC methods for the measurement of high molecular weight PAH in combustion-related samples (DoE) (see Technical Report 19), use of LC fractionation to isolate radiolytic products in irradiated meats (USDA), and the determination of PAH in marine sediments (NOAA).

Four new staff members and guest scientists have joined the LC Group during the past year. Barbara J. Koster joined the Group with responsibilities for the operation of and coordination of the activities in the Environmental Specimen Bank facility; Professor Zeng-nan Zhou from the East China Institute of Textile Science in Shanghai has joined the Group as a guest scientist working in the development of methods for water soluble vitamins in food matrices; Apryll M. Stalcup, a graduate co-op from Georgetown University, will investigate solute retention mechanisms in both LC and supercritical fluid chromatography; Professor Barry K. Lavine, a guest scientist from Clarkson University, is providing the Group and the Division with expertise in multivariate analysis; one staff member, Walter F. Kline, left NBS to accept a position in industry.

During the next several years, research in the understanding of LC retention mechanisms will continue to focus on (1) methods of physical and chromatographic characterization of stationary phases, (2) factors affecting selectivity, and (3) comparison of LC and SFC. 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 with emphasis on the polar constituents. In the coming years, we anticipate more emphasis on the measurement of vitamins in serum and food matrices and drugs of abuse in urine. In addition to analytical separations, LC will become more important as a means of isolating the analytes of interest from the serum or urine matrices prior to quantification by other techniques.

We intend to actively recruit postdoctoral research associates and guest scientists with backgrounds in retention mechanisms, bonded phase characterization, microbore/capillary LC, LC detector development, and/or supercritical fluid chromatography.

Stephen A. Wise, Group Leader; Bruce A. Benner, Jeanice Brown-Thomas, Richard G. Christensen, Barbara J. Koster, Barry K. Lavine, Sam A. Margolis, Lane C. Sander, Apryll M. Stalcup, J. Sullivan, and Zeng-nan Zhou.

5. Mass Spectrometry Group: Overview

The Mass Spectrometry Group conducts research in a number of areas including both basic and applied efforts. The major part of our work continues to be in the development of mass spectrometric methods for the accurate quantitation of individual organic compounds in complex matrices and in the laser-induced photodissociation of ions as part of the mass spectrometry competence building program, "Analysis of Ionization Mechanisms and Ion Structures."

Quantitative measurements made in the mass spectrometry group in the past year have been used in the certification of several SRMs as described in Technical Report 26. We also contributed to an international round robin on the determination of polynuclear aromatic hydrocarbons (PAH) and nitro-PAH. The results are reported in Technical Report 25. The research reported in previous years on the behavior of PAH and substituted PAH in negative ion chemical ionization has been extended and applied (Technical Report 12), to the determination of some PAH and substituted PAH in the extract from urban air and diesel exhausts particulates.

The use of isotope dilution and GC/MS in developing definitive methods for quantitative determination of constituents in human serum has continued in collaboration with the Bioanalytical Techniques Group. A new and substantially simplified method developed for uric acid is described in Technical Report 15. The method for cholesterol is being applied to several serum pools, distributed to clinical laboratories by the College of American Pathologists as part of their proficiency testing program, in an effort to resolve a discrepancy between the mean results of the clinical laboratories and those of the Centers for Disease Control's reference method. Work on a method for "triglycerides" has been deferred in favor of developing a method for vitamin C (ascorbic acid).

The isotope dilution methodology developed for the definitive methods has been adapted and extended to low concentrations for the determination of 3-quinuclidinyl benzilate (BZ), a chemical agent scheduled for demilitarization, and its metabolites as described in Technical Report 13. This isotope dilution GC/MS approach is also being employed in a joint effort with the Center for Radiation Research for the Department of Agriculture. We are investigating the feasibility of monitoring certain oxidation products of amino acids formed in fresh meat exposed to ionizing radiation as a means of determining the radiation dose to which the meat was exposed. This work is described in Technical Report 14.

Investigation of the laser-induced photodissociation of both positive and negative ions generated by cesium ion bombardment, done as part of the competence building program in mass spectrometry, has continued successfully, demonstrating that the technique has potential for the determination of the structure of large molecules. The results are summarized in Technical Report 11.

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 method for the determination of BZ; the development of SRMs with certified concentrations of metabolites of cocaine and marijuana in urine, the development of methods for the determination of polar compounds in air and diesel particulates and for radiolytic products in meats to determine radiation dose; the completion of a definitive method for vitamin C; the application of the new method for uric acid; the improvement and application of the definitive method for cholesterol to a number of serum pools as our contribution to the development of a National Reference System for Cholesterol, and, as part of the mass spectrometry competence building program, increasing the extent of photodissociation achieved and investigating the chemical modification of molecules of biological interest to permit photodissociation with visible light. Longer range plans include: the development of SRMs for cholesterol at high levels; the development of definitive methods for triglycerides in serum and for analytes in matrices other than serum; the extension of the post-irradiation dosimetry program to include non-meat products and to investigate loss of nutrient content as a function of dose; the development of a triple quadrupole mass spectrometer for high accuracy quantitation; and the adaptation of photodissociation experiments to instrumentation other than the high resolution double focusing magnetic instrument presently used.

The age and limitations of our instrumentation has been and remains a concern. During the past year, a quadrupole GC/MS instrument was retired, and a triple quadrupole instrument, no longer useful for analytical measurements, was permanently loaned to the Chemical Kinetics Division, Center for Chemical Physics. The group presently has five mass spectrometers; two of these instruments have proved difficult to keep operating this past year. The expected acquisition of a modern, fully equipped, triple quadrupole instrument in 1987 will provide additional GC/MS capacity and substantial new analytical capability.

John-Marc Rodier, a student at The American University, has joined the group for the summer to assist with the photodissociation experiments and to run service analyses. He is expected to return next summer. We are seeking postdoctoral candidates whose interests are compatible with our programs and are particularly interested in finding a strong candidate for the photodissociation work. We are also in need of and seeking an additional person for the drugs in urine SRM work.

Edward White V, Group Leader; Gary D. Byrd, Polly Ellerbe, Laurence R. Hilpert, Stanley Meiselman, Larry R. Phillips, John-Marc Rodier, Lorna T. Sniegoski, and Michael J. Welch.

B. Selected Technical Reports (Organic Analytical Research Division)

1. Analysis of Electrophoretic Protein Patterns of Human Liver

J.J. Edwards

The Bioanalytical Techniques group has undertaken the task of establishing two-dimensional polyacrylamide gel maps of selected human tissue proteins. The initial effort is directed toward mapping non-pathological tissue samples in order to begin generating a data base of normal proteins present in the population. Presently the tissue under study is human liver obtained from the NBS/EPA Environmental Specimen Bank. To date we have examined five liver specimens by this protein mapping technique. These samples were from individuals in the age range 18 to 57 years and included three males and two females.

Because we are not presently equipped to obtain a computerized analysis of the protein maps, we used the services of Protein Data Bases, Inc. (Huntington Station, NY) to provide the initial computer gel matching services. The computer gel matching involved the scanning, digitization, smoothing and storage of two film exposures of each gel pattern. From this information, composite images of each gel were created. Confirmed protein spots were assigned position numbers which were used in subsequent matching experiments. Quantification was accomplished by conversion of the optical density of each protein spot to the relative amount of protein represented by that image. Quantification data were presented in the form of bar graphs in order that individual spots in each sample could be compared. Approximate molecular weight and isoelectric point data were also provided.

One sample was arbitrarily chosen as a "standard" for comparison to the other samples. This sample was found to contain 472 resolved protein spots. Overall, individual samples contained between 362 and 473 resolved spots with a total number of 594 different spots being detected.

Using this information as a starting point, we can assess our in-house capabilities for gel imaging and protein quantification, and establish a measurement base against which other protein samples can be compared. The information obtained concerning protein electrophoretic patterns from "normal" tissue samples will also be of interest to other researchers in several diverse fields such as biotechnology, environmental toxicology and separations science.

2. Analytical Studies of Commercial Sources of Sodium Dodecyl Sulfate

M.C. Kline and D.J. Reeder

Electrophoretic separations of proteins can vary depending upon the source of sodium dodecyl sulfate (SDS) utilized in the system. In many instances the different sources of SDS may have the same composition by chain length analysis, but behave quite differently in their ability to solubilize proteins. Analytical tests were performed on 18 different lots/sources of SDS to determine the presence or absence of factors other than chain length that may be associated with the quality of electrophoretic separation. These include:

pH: The pH of a 1% aqueous solution of the SDS samples ranged from 5.8 to 9.5, demonstrating the non-uniform nature of these samples.

Conductivity: The conductivity of a 1% aqueous solution of the SDS samples ranged from 1140 to 1629 siemens.

HPLC: HPLC analyses of the 1% aqueous solution of the SDS samples utilizing a C_{18} column in conjunction with a conductivity detector were performed. Total peak areas of the chromatograms ranged from 3.11 to 5.46 cm^2. HPLC analysis for the presence of free alcohols in the SDS samples was achieved by quantitatively derivatizing the free alcohols with 1-naphthylisocyanate and chromatographing the derivatives on a C_{18} column, monitoring the absorbance at 230 nm. Free decanol, dodecanol, tetradecanol, and hexadecanol in the samples ranged from 0.013% to 0.419% with decanol varying from 0 to 0.106%; dodecanol from 0.006% to 0.245%; tetradecanol from 0 to 0.116%; and hexadecanol from 0 to 0.111%.

Critical Micelle Concentration (CMC): CMC values for 7 of the SDS samples were established by a spectroscopic dye method. These values ranged from 0.010 to 0.022 g/L. The remaining samples are being evaluated.

Electrophoretic separations are now being performed on a standard protein sample using the different SDS samples. After these separations are complete, we will attempt to discover correlations between the analytical data and the electrophoretic patterns. This work should provide researchers using electrophoresis with the basis for making choices in their selection of reagents for protein separations based on reagent components.

3. NMR Characterization of Solid Sugars for Use in Measurements of Enthalpy of Combustion

B. Coxon, J.C. Colbert, and E.S. Domalski

In a collaborative project in biotechnology with personnel of the Center for Chemical Physics, both liquid- and solid-state NMR techniques have been used to determine the anomeric compositions of crystalline D-ribose and 2-deoxy-D-ribose (2-deoxy-D-*erythro*-pentose) samples that were to be used in measurements of enthalpy of combustion and enthalpy of formation. This study was initiated in order to increase understanding of the energetics of chemical bonding in nucleosides and nucleotides. Information on the anomeric compositions of the solid sugars was required so that the measured enthalpies could be correctly attributed to either a single anomeric ring form, or to a mixture of anomers. Such information is generally not available without analytical investigation, because, depending on the physical and conformational properties of the sugar and on the conditions of crystallization, sugars may crystallize principally either as a single ring form, or as a mixture of two-to-four anomeric ring forms and an acyclic *aldehydo* form. These forms may equilibrate during melting of the sugars, as has been experienced during differential scanning calorimetric (DSC) measurements. This behavior is also relevant to understanding phase transition phenomena in sugars, as well as to mechanisms of combustion.

Several investigations at NBS have suggested that the compositions of *solid* sugars (for example, SRM D-glucose) and certain other related materials (for example, pyruvate cyclic dimer) can be determined by dissolution in dimethyl sulfoxide-$\underline{d}_6$ (DMSO-$\underline{d}_6$), followed by analysis of the resulting solution by ^1H or ^{13}C NMR. In this solvent, isomerization is usually sufficiently slow that the proportions of different forms determined soon after dissolution are a good indication of the compositions of the solid materials. The relative proportions of the four ring forms of D-ribose and 2-deoxy-D-ribose have been measured by digital integration of the HO-1 doublets in the ^1H NMR spectra of solutions of both the crystalline and the melted sugar samples. The applicability of the solution method has been confirmed by direct analysis of the crystalline sugars by cross-polarization--magic angle spinning (CP-MAS) ^{13}C NMR spectroscopy (courtesy of D. Vanderhart). The results from the two NMR methods have been compared and they indicate that the crystalline D-ribose is principally a mixture of 64-65% of the β-pyranose (β-p) form and 34-35% of the α-pyranose (α-p) form, whereas crystalline 2-deoxy-D-ribose is almost exclusively the β-p form.

The thermochemical, NMR, and DSC results have been submitted to the Journal of Chemical Thermodynamics.

4. Immobilized Enzymes Bound to Inert Supports Retain Activity

M.C. Kline, D.J. Reeder, P.V. Sundaram, and P. Vetter

One component of the biotechnology initiative funded by Congress during the past year involves the investigation of mechanisms of enzyme stabilization and protein activity. One approach to the solution of this problem involves covalently binding proteins at sites remote from the active site. As a beginning to this work, we have immobilized the enzyme, urease, on a variety of different inert supports by diverse coupling mechanisms. The retained enzyme activity of small columns packed with immobilized enzyme varies from support to support and also seems to vary with the coupling technique used.

Retained enzyme activity of the columns over time is being studied using a spectroscopic assay. At present there are 8 columns that have been studied for 32 weeks. Five columns have retained between 76% to 87% of their original enzymatic activity. Another column has retained 17% of its original activity while the remaining two columns have only 1% or less retained activity. In addition to the above columns, there are 7 additional supports that have been recently synthesized. Three of these columns are retaining their enzymatic activity (76% after six weeks).

Supports made of Nylon derivatives seem to be better suited as immobilization sites than do those of the more popular carboxymethyl-Sephadex. Tosylation and tresylation coupling methods appear to be the preferred procedure for retaining urease activity on the nylon supports.

Additional studies will focus on new chemistries for linkage and on the use of enzymes that may have use in industrial biotechnology applications. Scale-up to larger column bed volumes will be attempted once the reactions are characterized.

5. Honey Protein Patterns from Isoelectric Focusing Allow Classification by Origin

F.R. Guenther, D.J. Reeder, and K.L. Richie

In a previous report (Technical Activities, Center for Analytical Chemistry, 1985, p. 113), a collaborative study with the Food and Drug Administration (FDA) is described wherein ultra-thin isoelectric focusing and two dimensional electrophoresis were used to compare protein patterns in honey that originated in the United States, Argentina, Hungary and China. Using ultra-thin (160 μm) polyacrylamide gels followed by a silver staining method for protein visualization, we found that there were significant differences in the protein patterns in the honey of the four countries.

To pursue this study in more detail, we decided that it would be necessary to limit our honey source to one country and instead examine several types of honey from different floral sources and geographical regions in the United States. We examined 40 honey samples provided to us by the Food and Drug Administration which represent several different floral sources and three geographical locations--California, North Dakota and Florida. Sample preparation involved dialysis, centrifugation, and adjustment to a constant protein concentration. Ultra-thin isoelectric focusing was used as our primary method of separation, followed by silver staining for protein detection. At this stage of analysis, all honey samples appeared to give very similar protein band patterns with the average (pI) values ranging from 4.9-5.8. To probe further, we used laser densitometry and pattern recognition programs so that we could analyze the information encoded in the protein composition of honey.

All data from the laser scans including peak area and relative band position were entered into a microcomputer (Lotus) spread sheet and the data were analyzed with a microcomputer based statistical program (Statpro) or transferred to the NBS computing facility for further statistical analysis with the ARTHUR chemometrics/statistical software package for mainframe computers. Pattern recognition procedures within ARTHUR were run on scaled protein data to determine if there were significant regional differences encoded in the protein patterns. Using several of these pattern recognition programs we were able to correctly classify the samples according to their origins. Thus it appears that information regarding geographical source of origin was encoded in the protein patterns. Classification of the data based on the floral source of the honey was also attempted. However, these analyses suffered from the lack of enough cases for each floral source.

More work is planned to demonstrate further the capabilities of combined high resolution protein separations and state-of-the-art data analysis procedures. We also anticipate studies to analyze more honey to see if classification based on floral source is possible.

6. Development of Bioanalytical Sensors

L.L. Brown, R.A. Durst, R.M. Kannuck, and A.L. Plant

Biologically derived substances such as antibodies, cell-surface receptors and circulating binding proteins have important application as components of rapid sensing devices because of their binding specificity, the strength of their interactions, and their potential for use in a wide variety of detection schemes. We are currently exploring optical and electrochemical techniques for detection of low levels of analyte based on immunological recognition. The binding of analyte to antibody results in a change in fluorescence or electrochemical signal by release of indicator substance from liposomes. Liposomes are phospholipid bilayer membranes which enclose an aqueous volume in which such indicator agents are trapped. We have found that ferrocyanide is an excellent agent for electrochemical detection, and cannot be detected until it is released from inside liposomes. It can be trapped in liposomes at high concentrations (10^{-3} M) with minimal spontaneous leakage. For fluorometric detection, we have used 5-carboxyfluorescein and other xanthene dyes which are approximately 95% self-quenched in vesicles at local concentrations of 100 mM.

Release of these dyes from liposomes results in dilution and increase in fluorescence intensity. The use of liposomes amplifies the sensitivity of the system because for every antigen-antibody binding event which occurs on a liposome surface, thousands of indicator molecules are released. Both a homogeneous and a heterogeneous assay are being developed using antibodies to 2,4-dinitrophenol (DNP), a model hapten, and DNP-aminocaproyl phosphatidylcholine, which is a component of the liposome bilayer. In the homogeneous assay, binding of anti-DNP antibody to the DNP on liposome surfaces initiates, in the presence of serum, release of the aqueous contents of the liposomes by serum components collectively known as "complement". In a flow injection heterogeneous assay, free antigen competes with antigen covalently coupled to the surface of liposomes for binding to antibody which is covalently coupled to a solid support. The number of liposomes displaced from the solid support is proportional to the amount of analyte present. The displaced liposomes are collected downstream from the reaction chamber, disrupted with detergent, and their trapped contents are quantified.

The sensitivity of electrochemical detection to be used in both assays is enhanced by the use of a polymer modified electrode. The reaction of 4-[2-(trichlorosilyl)ethyl]pyridine at an oxidized platinum surface results in the convalent bonding of the organosilane to the electrode. By refluxing in neat iodomethane, the pyridine is quarternized and acts as an ion exchange site for the anionic ferrocyanide. By this preconcentration of the analyte, sensitivity of the technique is increased by about two orders of magnitude. The use of this polymer modified electrode also prevents fouling of the electrode surface by serum proteins -- a common problem that has hindered electrochemical analysis in biological solutions. This feature is especially important to our development of a homogenous immunoassay involving complement-mediated lysis of the liposomes. The combination of high specificity for analyte with efficient amplification provides the potential for extremely sensitive devices with predicted detection limits of 10^{-14} M.

The use of liposomes in biosensors is an important means for providing chemical enhancement of biochemical reactions. One of the major areas to be studied with respect to liposomes is consistency in their preparation, homogeneity in their size, and stability with respect to their permeability and composition.

7. Chronoamperometry in Polymer-Modified Electrodes

W.T. Yap and R.A. Durst

In electroanalytical chemistry, the faradaic current produced by various applied potential techniques yields important information about the analyte. The measurements and analyses of the faradaic current in polymer-coated electrodes are complicated by the large charging current due to the high resistance and the capacitance of the system and, in addition to the usual ionic and molecular diffusion, by the effect of migration of charged species. In large potential step chronoamperometry, these complications give unusual current-time curves which are not simply of the inverse-square-root-of-time type for a simple diffusion-controlled case nor the exponential decay of an RC circuit; neither is it a simple superposition of the two. In order to elucidate these behaviors, we developed a digital simulation of this problem, using a finite element procedure which is especially convenient for cases with zero flux at the boundary. This problem has naturally two scales of time: RC, the decay constant of the charging current and d^2/D which is a measure of the transport time of the electroactive species with diffusion coefficient D through the thickness d of the polymer layer.

For RC<<d^2/D, the current-time plot may be approximated by joining the charging current for the RC circuit at short time with the transport-limited faradaic current when the charging current becomes negligible. As RC approaches d^2/D, the effect is not as simple, and working curves were constructed from the simulation.

By superimposing the experimental ln[current*sqrt(time)] versus ln(time) plot onto the theoretical working curves until they fit, some of the unknown experimental quantities, such as the diffusion coefficients, can be determined. This procedure was successfully applied to an electrode coated with poly$[Ru(II)(bpy)_2(4\text{-}vpy)_2]^+$ PF_6^-.

The effects of these and other electrode parameters on the charge-time behavior will be studied further to develop more useful diagnostic plots. For example, plots of cyclic voltammetric peak current ratios or peak separations as functions of the electrode parameters will be constructed for characterization or diagnostic purposes.

8. FTIR-Photoacoustic Spectroscopic Characterization of Thermally Crosslinked and Derivatized Poly(vinylpyridinestyrene) Copolymer Film Electrodes

E.A. Blubaugh, Jr. and C.K. Chiang

One of the goals of this research program is the development of electrochemical detectors for use with liquid chromatography. With solvents of varying nature and fluid flow past these electrodes, long-term stability of these electrocatalytic polymer films is of paramount importance. We have developed a thermal crosslinking procedure which enhances the stability of the bulk polymer film and the polymer film/substrate electrode interface by almost two orders of magnitude.

As part of this work, it was necessary to optimize the thermal crosslinking procedure with respect to the crosslinking agent, initiator, and time. These polymer film electrodes contain about 10 micromoles of polymer, and this polymer film/electrode combination is optically opaque. With these two conditions, transmission spectroscopic techniques are ruled out. However, FTIR-photoacoustic spectroscopy (FTIR-PAS) is ideally suited to examine samples such as ours. FTIR-PAS is a surface sensitive and, as important, nondestructive analytical method for determining the vibrational spectroscopic character or "finger printing" of these polymer films.

Our study began by obtaining the FTIR-PAS spectra of the polymer powder and the crosslinking agent as received. We then addressed the questions of whether the crosslinking agent was retained in the polymer film during the thermal treatment and, also, were the crosslinking active sites totally reacted. We found that the crosslinking agent was retained in the polymer films and that the active crosslinking sites where totally reacted. An additional piece of information that we obtained from this study was that the parent polymer is not degraded by our oxidative thermal procedure. The second question that we addressed was to determine if the spectrum of the polymer film changes as a function of film thickness. This is an important question since FTIR-PAS is a surface sensitive technique. The film thickness was varied from about 0.1 to 1 μm and an FTIR-PAS spectrum was obtained at each thickness. We did observe differences for the vibrational bands associated with the cross-linking agent as a function of thickness. At thin films we observe one IR band for the ester groups ($\sim$1730 cm^{-1}) and with thicker films we then observe three IR bands for the ester groups. This difference is presumed to be due to the heterogeneity of these polymer films. One possible explanation for the heterogeneity of these films is due to spatial differences imposed by some of the polymer macromolecules being near the platinum surface and some being far from the platinum surface.

Future work with FTIR-PAS as a tool to study these polymer film electrodes will focus on immobilizing different metal complexes and studying the binding of these complexes as well as studying the binding of these complexes in the films. This will help to determine if immobilization is via covalent linkage or just due to simple entrapment.

9. Catalytic Oxygen-Scrubber Column Developed for the Reductive Electrochemical Detection of Nitro-PAH in Diesel Soot

W.A. MacCrehan and S.D. Yang

The need to remove oxygen from the mobile phase for reductive electrochemical detection in LC has limited the application of this powerful technique. Although many schemes for oxygen removal by complete purging of the solvent reservoir, degassing with oxygen-permeable tubing, or even chemical reduction with a zinc-scrubber column, have appeared in the literature, none has gained widespread use. We have developed a different approach, conceptually similar to the work of Tejada et al. at EPA Research Triangle Park, that uses a catalytic reaction of alcoholic solvents with the mobile phase oxygen. Oxygen reduction occurs in a 15 cm column packed with a platinum catalyst which is incorporated into the LC system after the solvent delivery pump. Complete reduction in the presence of methanol is evidenced by the low residual current observed at mercury thin-film electrodes in the potential range of 0 to -1.2 V (vs. Ag/AgCl). We have also examined the residual current at two potentials (-600 and -1000 mV) as a function of the percentage methanol in the mobile phase. As little as 1% methanol provides some reduction of oxygen, but 3% is required for low residual currents.

The convenience and efficacy of the Pt oxygen scrubber was demonstrated in the reductive determination of nitro-polycyclic aromatic hydrocarbons (N-PAH) in extracts of diesel particulate matter (soot). We have investigated two approaches to the problem of achieving the selectivity to measure the N-PAH in this very complex matrix. In earlier work, we used the differential-pulse (DP) mode of detection to increase the detector selectivity, so that sample fractionation was not necessary. However, because of the unusual sensitivity of the electrochemical signal to the detection conditions for N-PAH, the reproducibility with this approach is poor. We had not observed the reproducibility problems with simple amperometric detection, so the second approach we have pursued this last year to achieve adequate selectivity to determine the N-PAH in this complex matrix is a two-step prefractionation of the soot extract. First, a hexane/methylene chloride extract is solvent extracted with concentrated aqueous ammonia to remove many interfering acidic components. The organic layer is collected, evaporated, redissolved, and then sorbed onto a small normal phase (silica) sample preparation cartridge and eluted with hexane:methylene chloride. This fractionation procedure removes many of the interfering reducible matrix compounds (such as PAH-quinones). Then, using a simple isocratic solvent program with the amperometric detection, baseline-resolved signals for the 1-nitropyrene and its deutero analogue can be achieved. Results on the determination of 1-nitropyrene in a diesel soot sample certified recently as SRM 1650 by the new LC/EC technique are in agreement with independent measurements by GC/MS and LC/FL.

10. Determination of Biogenic Thiols Using HPLC with Electrochemical Detection

D. Shea and W.A. MacCrehan

A variety of organic sulfur compounds are produced in marine sediments by microbial sulfate reduction and digenesis of organic matter. Thiols are of particular importance because they are major intermediates in the microbial cycling of sulfur and also have a high affinity for certain trace metals. Despite the biogeochemical significance of thiols, relatively little is known about the nature and distribution of these species in marine waters and sediments. In order to evaluate the role of thiols in marine processes, we are developing methods for the determination of biogenic thiols and disulfides in natural water samples.

Initially, we have been using a reverse-phase, ion-pairing HPLC separation coupled to selective electrochemical detection at a gold/mercury-film electrode. This method has been found to be both sensitive and selective for many thiols when analyzing standards. However, we have encountered some difficulties with the most hydrophilic thiols (e.g., cysteine) when analyzing natural water samples. Therefore, we are currently investigating a method using precolumn derivatization of the thiols with *o*-phthalaldehyde to form isoindole products. The major advantages of this method are increased retention of the hydrophilic thiols and the capability of detecting the thiols with both electrochemical and fluorometric detection. We are in the process of analyzing sediment pore water samples from the Chesapeake Bay with both of these HPLC methods.

With the development of a reliable method for determining thiol concentrations in natural waters, we are poised to investigate the effect of thiols on trace metal mobility in the marine environment. Efforts to account for observed trace metal concentrations in anoxic marine waters have had only limited success in the past, due in part to the lack of knowledge of the identity and amount of thiols that are present. There have been no previous attempts to measure trace metal concentrations simultaneously with the inorganic and organic sulfur species in marine waters. In addition to the thiol measurements, we will be using standard polarographic methods for the determination of the inorganic sulfur species (sulfide, polysulfide, sulfite, thiosulfate and polythionates) and certain trace metals (Cu, Cd, Zn, and Pb). These data will be used to develop a thermodynamic model describing the solubility of sulfide minerals in marine waters.

11. Photodissociation of Ions Generated by Liquid SIMS

M.J. Welch and E. White V

New "soft ionization" techniques have permitted the mass spectrometric analysis of many biomolecules and other thermally labile and nonvolatile compounds. Soft ionization is a term used to describe processes in which gaseous ions are formed with little excess internal energy. Such ions tend to remain intact, resulting in mass spectra exhibiting strong $[M+Adduct]^+$ ions and little fragmentation. Since fragment ions provide structural information, approaches have been developed for inducing fragmentation of ions generated by soft ionization techniques.

The most common approach has been the use of collision induced dissociation (CID), in which the ions are excited by collisions with gaseous molecules and then dissociate. An alternate approach is photodissociation, in which the ions are irradiated with photons. If the photons are absorbed, the ions are excited and may dissociate. This technique has two potential advantages: 1) the energy input to an ion can be better controlled than with CID; and 2) photodissociation is only observed for those ions that absorb photons, thus certain substances can be photodissociated selectively in the presence of others by proper choice of wavelength.

We have investigated the photodissociation of ions generated by bombarding a liquid matrix with high energy cesium ions, an ionization technique known as liquid SIMS. An argon ion laser is used to irradiate the first field-free region of a double-focusing mass spectrometer. Ions that are formed by dissociations of a selected parent ion in this region are detected by means of a linked scan at a constant ratio of the magnetic field strength to the voltage on the electrostatic analyzer. The laser beam is mechanically chopped and ions formed in-phase with the chopped light are detected by a lock-in analyzer. We have now studied the photodissociation by visible light of both positive and negative ions formed by cesium ion bombardment of a variety of substances to determine if useful structural information can be obtained.

The compounds tested for evidence of photodissociation had molecular weights ranging from about 250-1400 u. We have observed that for compounds in this range, the absorption spectra for gaseous molecular ion species is very similar to that of the condensed phase material. Thus compounds which absorbed strongly in the 450-515 nm range exhibit the strongest photodissociation for both positive and negative ions. Such compounds are generally red or orange in color. Methyl red, for example, exhibits a moderately intense photodissociation mass spectrum, which is distinctly different from the CID spectrum. Other compounds which are highly colored in a different portion of the visible spectrum generally exhibit weak photodissociation, while colorless compounds exhibit no photodissociation. The results of the photodissociation of positive ions was recently published (Anal. Chem. 58, 890-894, 1986). For negative ions, electron detachment is a competitive process with photodissociation. While we are unable to measure the amount of electron detachment that occurs, we can estimate its relative effect by comparing the abundance of daughter ions formed by photodissociation with the total loss of abundance of the parent ion. We found that if the daughter ion formation is large, the relative amount of electron detachment is small, but it becomes the major factor if the compound being tested exhibits low daughter ion production.

The technique is limited on our present instrumentation by the short interaction time between ions and photons. It is also limited by the lack of an intense uv source in the 200 nm region, where most substances absorb. We are investigating the attachment of groups with chromophores for visible light to colorless molecules, such as peptides, to determine if structural information can be obtained. The combination of a fourier transform mass spectrometer, which allows ions to be stored and irradiated for up to a few seconds, with an excimer laser, which provides intense pulses of uv light down to 190 nm, appears to be the most promising approach to making this technique a useful structural tool.

12. Determination of PAH and Alkylated PAH in Particulate Extracts Using Negative Ion Chemical Ionization Mass Spectrometry

L.R. Hilpert

An interesting aspect of the negative ion chemical ionization (NICI) mass spectrometry of polycyclic aromatic hydrocarbons (PAH) is the selectivity of detection observed for certain isomeric species. Two striking examples of this are the selectivity of detection observed for the molecular anion ($M^{-\cdot}$) of fluoranthene over pyrene, and the selectivity of detection of $M^{-\cdot}$ for benzo(a)pyrene over benzo(e)pyrene. Under optimized conditions of ion source pressure and temperature, the molecular anion for fluoranthene is more than 100x more abundant than that of pyrene, and the molecular anion for benzo(a)-pyrene is more than 1000x more abundant than that of benzo(e)pyrene. In addition to the selectivity of detection observed for the parent PAH, similar selectivities are seen for their alkylated homologues. As many alkylated PAH are known to be as mutagenic as the parent PAH, and in some cases more so (e.g., chrysene is only weakly mutagenic, whereas 5-methylchrysene is as potent a carcinogen as benzo(a)pyrene), sensitive analytical methods capable of determining alkylated species at low concentrations in complex mixtures are needed. NICI has proven to be a useful mass spectrometric technique for solving the difficult problem of differentiating isomeric PAH species.

During the past year NICI and EI mass spectrometry were used for the determination of PAH and alkylated PAH in two particulate samples which have previously been certified as Standard Reference Materials: SRM 1648, Urban Particulate Matter, and SRM 1650 Diesel Particulate Matter. Using a combination of EI and NICI techniques, it was possible to differentiate and quantify individual isomeric PAH and alkylated PAH based on the selectivity of detection under NICI conditions. Methyl-substituted fluoranthenes were easily distinguished from methylpyrenes, and methylbenzo(a)pyrenes and methylbenzofluoranthenes could be distinguished from the methylbenzo(e)pyrenes.

Under EI conditions both methylfluoranthenes and methylpyrenes are detected in the selected ion monitoring analysis. Under NICI conditions however, fluoranthene and the methylfluoranthenes are detected selectively. No peaks due to pyrene or the methylpyrenes are observed. Comparison of the EI and NICI analyses allows facile identification of the methylfluoranthenes and the methylpyrenes.

Methyl-substituted benzo(e)pyrenes could also be distinguished from other methyl-substituted MW 252 isomers (methylbenzofluoranthenes, methylbenzo(a)-pyrenes, or methylperylenes) using NICI. Although the situation was somewhat more complicated by the fact that there are more MW 252 species which give a NICI response, it was possible to identify three different methylbenzo(e)-pyrenes in extracts of the air and diesel particulates.

Results from the quantitative measurement of alkylated PAH showed that the methylfluoranthenes were present at approximately 17 μg/g in the diesel particulate sample, which represents approximately 33% of the fluoranthene concentration (51.0 μg/g). The methylpyrenes were also present at approximately 30% of the pyrene concentration. In the air particulate sample, the methylfluoranthenes were present at 2.5 μg/g, which represents approximately 30% of the fluoranthene concentration (9.2 μg/g). The methylpyrenes, at 1.3 μg/g were 18% as abundant as pyrene (7.3 μg/g) in the air particulate sample. The methylbenzofluoranthenes and methylbenzo(a)pyrenes were present at approximately 30% of the concentration of the parent PAH in the diesel particulate SRM, and at approximately 12% of the parent PAH concentration in the air particulate SRM.

In addition to the selectivity advantage offered by NICI, it is well suited for the quantitative determination of alkylated PAH due to the greater sensitivity for those compounds which are NICI sensitive. Also, response factors for alkylated PAH are essentially the same as for the parent PAH under NICI conditions, unlike EI where there may be large differences in response factors for isomeric alkylated PAH. This enables reliable quantitative results to be obtained, even in the absence of authentic standards for the individual isomers. In this regard, work is currently underway on the NICI determination of nitrated PAH and alkylated nitrated PAH (for which there are few authentic standards available) in the diesel and air particulate samples.

13. Development of a Confirmatory Chemical Test for Exposure to 3-Quinuclidinyl Benzilate (BZ)

G.D. Byrd, L.C. Sander, L.T. Sniegoski, and E. White V

The current stockpiles of the incapacitating agent 3-quinuclidinyl benzilate (BZ) in the U.S. are scheduled for demilitarization in the near future. Because of the potential for worker exposure to this material, the U.S. Army Medical Research and Development Command is supporting the development of a confirmatory test for human exposure to BZ prior to the start-up of the actual demilitarization process. The purpose of this project is to develop a highly specific confirmatory test based on an evaluation of the literature and from research conducted by NBS. We are developing a method for this test using isotope dilution GC/MS analysis of urine sample extracts.

BZ is a relatively nonvolatile ester that affects the brain and nervous system. It is a specific binding antagonist for the muscarinic class of receptors and is capable of producing incapacitation at very small doses (1-5 ng/g). Of the BZ that enters the body, 50 to 90% is excreted via the kidneys with most in the form of the metabolites benzylic acid (BA) and 3-quinuclidinol (Q). The exact relationship between BZ dose and levels of BZ, BA, and Q in the urine is not well understood. However, based on the known no-effect level, the required detection limits of these analytes in urine have been set at 0.5 ng/mL for BZ and 5 ng/mL for BA and Q.

Confirmation of specific exposure to BZ requires that the analysis be for intact BZ or for both BA and Q. A method for quantifying all three analytes is desirable. Initial work on this project has focused on the metabolites BA and Q. Isotope dilution GC/MS was selected as the analytical method because of the need for high sensitivity and selectivity for these analytes in a complex matrix. Labeled analogs of BZ, BA, and Q were synthesized in order to do the isotope dilution measurements.

BA was extracted directly from urine with chloroform. Q, on the other hand, proved difficult to extract from urine into organic solvents due to its polar and hydrophilic properties. A method using a Florisil SepPak^{TM} cartridge was developed to remove the Q from urine. The Q was eluted from the cartridge with concentrated NH_4OH. The extracts from both samples were dried and derivatization reagent was added to each to form the trimethylsilyl derivatives of the analytes (BA-TMS and Q-TMS). The recovery of each analyte from urine is approximately 50% at the 5 ng/mL level.

The GC/MS instrument used was equipped with a 30 meter DB-17 fused silica capillary column directly interfaced to the source of a quadrupole mass spectrometer. Analyses were carried out by single ion monitoring (SIM) using the most intense ions above m/z 100. The fragment ion $(C_6H_5)_2COTMS^+$ at m/z 255 was monitored for BA-TMS and the molecular ion at m/z 199 was monitored for Q-TMS. This work demonstrates that the BZ metabolites BA and Q can be determined at the 5 ng/mL level in urine. Future work will involve the development of a method for detecting BZ in urine pending approval of our laboratory for handling exempt surety material.

14. Determination of the Relationship between Dose and Yield of Radiolytic Products in Irradiated Meats

W.A. MacCrehan, S.A. Margolis, W.E. May, M.J. Welch, S.D. Yang,
M. Dizdaroglu, L. Karum, and M. Simic

Treatment of foods with ionizing radiation to improve its storage lifetime is of considerable interest to the food processing industry. Proof that certain foods have or have not been irradiated will be required of food processors and wholesalers by regulatory agencies for regulating imports/exports. Reliable measurement methods for performing post-irradiation dosimetry are therefore needed by regulatory agencies also.

In a joint effort with the Center for Radiation Research (CRR), we are investigating the development of a method based upon production of certain amino acids in meat exposed to radiation. Phenylalanine, a common amino acid in protein, reacts with OH radicals formed in water by ionizing radiation to form isomers of tyrosine. Para-tyrosine is naturally present in meats at relatively high levels (low ppm), but the ortho and meta isomers appear to be present only at very low levels. Researchers in CRR have found that, at least in chicken meat, these two isomers may be completely absent from meat fibers, unless the meat has been irradiated. Therefore, our efforts are concentrating on determining if the formation of either of these two compounds can be correlated with the radiation dose. Other marker compounds which are under study, but appear less promising at this time, include two isomers of dihydroxyphenylalanine (DOPA) formed by irradiation from para-tyrosine and various compounds produced by irradiation from tryptophan.

Investigations involving the HPLC-UV analysis of radiolytic products from aqueous solutions of phenylalanine and para-tyrosine found a linear and reproducible relationship between the production of the o- and m-tyrosine isomers and the radiation dose, but the results for DOPA were much more scattered, possibly because of the instability of DOPA in solution. Direct HPLC-UV analysis of meat-based samples is not feasible. The most promising approach for the analysis of such samples involves use of a deuterated internal standard, hydrolysis of the sample under strong acid conditions, isolation of the amino acids of interest by HPLC fractionation, derivatization, and measurement by GC/MS with selected ion monitoring. Experiments with an unfractionated meat hydrolyzate found that production of the tyrosine isomers increased versus dose, while the DOPA isomers were not detected.

Work will continue on development of methods for the determination of radiation dose based upon the formation of radiolytic marker compounds in a variety of meats. Our efforts initially will concentrate on pork, for which radiation treatment is being considered to kill trichinae. At the present time we are investigating optimum conditions for HPLC fractionation. Other experiments to be performed involve determining the distribution of the marker compounds in unirradiated meats, the reproducibility of their production in irradiated meats, and the effects of temperature, dose rate, and storage conditions upon the concentrations of the marker compounds.

15. Development of a New Definitive Method for Uric Acid

A. Cohen, P. Ellerbe, S. Meiselman, R. Schaffer, M.J. Welch, and
E. White V

As part of our program for developing definitive methods for organic serum constituents, we have developed a new isotope dilution mass spectrometry (IDMS) method for the measurement of uric acid in human serum. The original method, developed ten years ago, gave satisfactory results, but the derivatization led to the formation of several isomeric tetraethyl uric acids and required a complex time-consuming sample workup. Other reported IDMS methods for uric acid are not sufficiently precise for our purposes or have not been tested for column memory effects or measurement bias. The new method for uric acid uses a simplified chemistry and sample workup, and is more precise than the original method. A new method for switching between the masses used for measurement has been devised which gives excellent precision even on very narrow GC peaks.

In this new method a known weight of serum is spiked with a known weight of uric acid-1,3-$^{15}N_2$ dissolved in ammonium hydroxide, and is allowed to equilibrate overnight. The uric acid retained on passage over an anion exchange resin is eluted with acetic acid and the eluent freeze-dried. Standards are prepared by weight from solutions of unlabelled and labelled uric acid, and are freeze-dried. The uric acid from either sera or standards is converted with N-methyl-N-(t-butyldimethylsilyl)trifluoroacetamide containing 1% imidazole in acetonitrile to the tetrakis(t-butyldimethyl-silyl)derivative. Samples and standards are introduced into the mass spectrometer via a 15 m DB-1 capillary column. Measurement of the unlabelled/labelled ratio for each sample is made in the electron impact mode by alternately monitoring the intensities of the $(M-57)^+$ ions at m/z 567 and 569. Samples are analyzed according to a strict protocol which involves running each sample with standards bracketing it in both time and ratio on two separate days. A test for column memory is included in each day's measurements; no evidence of column memory has been seen.

To accurately and precisely measure the unlabelled/labelled ratio for a GC peak, at least 30 measurement cycles must be acquired. Magnetic switching is too slow for our observed peak width of about 14 s, and accelerating voltage switching is too imprecise. We have devised a new system to switch between masses using the beam deflection plates located in front of the collector slit. With this system, repeated measurements of the ratio of a given mixture of labelled and unlabelled uric acid routinely give coefficients of variation of under 0.1%.

We prepared three independent sets of standards and tested them for consistency. The members of each set were used as standards for measuring the weight ratios of members of the other sets. The difference between the measured and weighed weight ratios was calculated as a percent difference, which was then used to calculate a mean bias between sets. The mean bias between sets was 0.15%, 0.10%, and 0.22% for each pair of sets.

To test for the presence of measurement bias, for example from an undetected interference, the measurements were repeated under different conditions. A test for bias was made monitoring the molecular ions at m/z 624 and 626. The difference between the weight ratios measured at M^+ and $(M-57)^+$ was 0.11%, which is within the precision of the measurements.

This new candidate definitive method for uric acid requires only minimal sample preparation, shows no GC column memory effect, gives excellent precision on repeated measurements of individual samples, shows acceptably low bias among sets of independently prepared standards, and shows no detectable measurement bias for serum samples. The method will be further investigated, and used to certify uric acid concentrations in reference serum pools.

16. Determination of Fat Soluble Vitamins using Liquid Chromatography with UV/Visible Absorbance and Oxidative Electrochemical Detection

W. A. MacCrehan and E. Schönberger

As part of an interlaboratory study sponsored by the National Cancer Institute (NCI), we have developed analytical techniques for the determination of retinol, alpha-tocopherol, and beta-carotene in human serum using reverse-phase liquid chromatography (LC) coupled to UV/visible absorbance (UV) as well as oxidative electrochemical detectors (EC).

Several aspects of the determination of these vitamins have been investigated: the organic solvent extraction; the choice of internal standards; separation of the vitamins and their isomers; selectivity of both the absorbance and electrochemical detection approaches; and the detection limits of the two detectors.

We have made notable improvement in the separation of the vitamins and their isomers, by using a polymeric, large-pore C_{18} column. We have also noted the benefit of the addition of n-butanol to the methanol/water (0.02 mol/L buffer) gradient system. Using a 35 minute gradient, all trans-retinol can be baseline separated from the 13-cis isomer; α-tocopherol can be separated from γ; and β-carotene can be separated from the α and 15,15 cis-isomers.

Oxidative amperometric detection has been developed as an alternative to UV for the measurement of retinol, α-tocopherol, and β-carotene. The hydrodynamic voltamograms indicate that all of these compounds may be detected at a glassy carbon electrode at an applied potential of +900 mV. A detailed comparison of the electrochemical and UV/visible absorbance detection approaches was made, with particular attention to the relative sensitivity and selectivity of the two detectors. EC detection provides comparable (carotene), better (tocopherol), and poorer (retinol) detection limits than UV. The selectivity observed with serum extracts is better for tocopherol but poorer for retinol and carotene.

The three vitamins were determined in several "round robin" serum pools in order to provide benchmark values for samples being analyzed as part of an NCI sponsored Micronutrient Analyses Proficiency Testing Program as well as in 40 split sera from an epidemiology study being conducted in Japan on atomic bomb survivors.

17. Characterization of Chemically Modified Substrates by Small Angle Neutron Scattering

L.C. Sander, C.J. Glinka, and S.A. Wise

Although liquid chromatography (LC) is now considered a mature analytical technique, the development of LC methods for analytical separations are often carried out on an empirical basis, without full understanding of the retention mechanisms involved. The selection of an appropriate column for a given separation is a case in point. Even among monomeric or polymeric C_{18} columns of the same type prepared by different manufacturers, variations can be great and separations that are easily achieved with one column may become difficult or impossible with other columns. These differences take the form of variations in column efficiency, absolute retention, and selectivity, and may result from differences in phase loading, the type of silane used in the synthesis, and trace metal activity and other differences in the silica substrate. For these reasons, the characterization of physical and chemical properties of bonded phase sorbents is of highest importance in elucidating such differences and the process involved in solute retention.

Small angle neutron scattering (SANS) is one technique well suited to the study of bonded phase morphology. In a collaborative effort with a scientist in the Institute for Materials Science and Engineering (C.J. Glinka), we have demonstrated the utility of SANS for the characterization of pore structure in bare silica substrates. Both surface area and pore size measurements determined by SANS were observed to correlate closely with values determined by other techniques. Furthermore, a procedure known as density matching was used to probe pore accessibility. By filling the pores of the bare silica with a solvent having similar scattering properties as the silica (in this case, a mixture of water and deuterated water), scattering from the sample was eliminated, thus proving the existence of a fully permeable pore network.

To obtain scattering information about alkyl modified substrates, a related density matching study was carried out using a mixture of methanol and deuterated methanol with C_8 and C_{18} modified controlled pore glass (CPG). The composition of the mixture was adjusted so that the scattering length density (sld; index of refraction for neutron scattering) matched that of (bare) CPG. The resulting scattering patterns were attributed to scattering from the alkyl layers. An analysis of the scattering patterns revealed that the pore network of the CPG was fully permeable to the methanolic mixture, even after silanization (no pore blockage). The scattering was found to be related to pore size of the CPG as well as bonded phase thickness. Because differences between the C_8 and C_{18} scattering patterns were evident, the "resolution" of the experiment is at least sufficient to discriminate between alkyl phase thickness differences of about 10 carbon atoms (ca. 1.5 nm). Development of mathematical models (based on the spinodal decomposition model for CPG) are in progress that should permit explicit evaluation of bonded phase thickness. Measurement of alkyl phase thickness of monomeric and polymeric C_{18} phases may ultimately lead to a description of solute retention processes that will aid column selection and method development.

The use of SANS to study bonded phases may also answer a controversial question about phase morphology: does alkyl chain conformation vary with solvent environment? Theory suggests that alkyl chains are closely associated with the substrate surface in polar solvents (collapsed state) and fully extended in nonpolar solvents (extended state). To test this theory, density matching experiments will be carried out in methanol, tetrahydrofuran, and toluene environments. Any changes in the resulting scattering patterns will be conclusive proof of phase conformational transitions.

18. Determination of the Molar Absorptivities of Bilirubin Isomers

R.C. Christensen

Natural bilirubin occurs as the IXα isomer. In the process of isolating preparations of bilirubin, some isomerization to the IIIa and XIIIa forms takes place. These isomers, IIIα, IXα, and XIIIα, can readily be separated by normal-phase liquid chromatography (1), but quantification of the relative amounts of each isomer present is not straightforward because the molar absorptivities of the isomers are different. If the molar absorptivities were known, however, at some given wavelength, the chromatography could be monitored with a variable wavelength UV absorbance detector, and the relative amounts of each isomer present could be inferred from the areas of the respective chromatographic peaks. Since the molar absorptivities of these compounds vary with the solvent it is important to know them in the solvent used as the chromatographic mobile phase.

Measurements of the molar absorptivity of these substances have been reported by McDonagh (2), and others have been made by A. Cohen and R. Burke in CAC. They are reported in chloroform, however, and at the wavelength of maximum absorbance, rather than all at the same selected wavelength. Therefore, it was decided to isolate a sufficient quantity of each isomer by semi-preparative liquid chromatography to enable us to determine the desired absorptivities.

Separations were carried out using a semi-preparative scale silica column with a mobile phase of methylene chloride containing 0.7% acetic acid. Fractions were collected from a number of runs, with the effluent being carefully filtered to remove silica particles from the column. Working in subdued light to inhibit photoisomerization, the solvent was evaporated. Each fraction was subjected to a refraction and the solvent was removed as before.

Analytical-scale liquid chromatography using a silica column, eluting with methylene chloride containing 2% acetic acid showed that the preparations had negligible contamination with the other isomers, with the exception of the XIIIα sample, which contained a small amount of the IXα isomer.

Molar absorptivities were measured at 23.6 °C at 452 nm in methylene chloride-2% acetic acid, making a correction for the IXα isomer present in the XIIIα isomer preparation. They were also measured in chloroform. Standard Reference Material 916, Bilirubin, was used as a photometric standard.

The millimolar absorptivities ($l\ cm^{-1}\ mmol^{-1}$) at 452 nm were found to be:

Solvent	IIIα	IXα	XIIIα	estimate of S.D.
CH_2Cl_2/CH_3COOH	68.26	61.93	51.42	0.52
$CHCl_3$	67.50	61.04	51.61	0.18

The absorptivities measured in chloroform were in good agreement with those found by others.

The determination of these values in conjunction with the use of the HPLC method described in reference (1) will assist analysts in making rapid, unambiguous assays of bilirubin samples for their content of these three isomers.

1. T.A. Woodbridge and D.S. Lightnor, J. Liquid Chromatogr. 1, 657 (1978).

2. A.F. McDonagh and F. Assisi, FEBS Letters 18, 315 (1971). (FEBS-Federation of European Biochemical Societies).

19. Determination of High Molecular Weight PAH in Coal Tar Air Particulate Materials

B.A. Benner, G.D. Byrd, A. Colmsjö, and S.A. Wise

The determination of polycyclic aromatic hydrocarbons (PAH) in environmental samples has focussed primarily on the measurement of PAH of molecular weight less than 300. Both capillary gas chromatography (GC) and reversed-phase liquid chromatography (LC) have been used extensively for these analyses. In general, the carcinogenic nature of complex PAH mixtures has been correlated with the concentrations of PAH of molecular weight 228 to 300 and, in particular, to the level of benzo[a]pyrene. However, Grimmer et al. (1) have shown recently that PAH of MW greater than 300 accounted for about 50% of the carcinogenicity of a hard-coal combustion effluent.

Recently, we reported the detailed characterization of PAH mixtures isolated from two Standard Reference Material air particulate samples (2). The PAH mixture was divided into subfractions based on the number of aromatic carbons. Of particular interest was the last fraction which contained a number of isomers of molecular weight 302 based on GC-MS analysis. The determination of PAH isomers of molecular weight 302, e.g., dibenzo- or naphthopyrenes, dibenzo- or naphthofluoranthenes, and benzoperylenes, has received relatively little attention for several reasons: [1] their low concentrations in samples of environmental interest relative to the lower molecular weight PAH, [2] the large number of possible isomers (34 isomers), and [3] the limited availability of authentic reference standards. In addition, GC is only partially successful in separating the numerous isomers and mass spectrometry provides little differentiation among the various isomers. Because of the above-mentioned limitations, the determination of these compounds in complex PAH mixtures has been generally limited to tentative identifications of one or two of these isomers based only on comparison with GC retention times.

Reference compounds were obtained for 19 of the possible 34 PAH isomers of molecular weight 302. Chromatographic retention characteristics were investigated for GC and LC (normal-phase LC on an aminosilane column and reversed-phase LC on both monomeric and polymeric C_{18} columns). In normal-phase LC these compounds have similar retention characteristics, thereby allowing isolation of these isomers as a group from complex mixtures. As with other groups of PAH isomers, polymeric C_{18} columns were found to have greater selectivity than the monomeric C_{18} column for the reversed-phase LC separation of these isomers. Reversed-phase LC on a polymeric C_{18} column was capable of separating all seven of the available dibenzo- and naphthopyrenes and seven of the ten dibenzo- and naphthofluoranthene standards. The elution order of these isomers on the polymeric C_{18} phase is closely related to the shape (length-to-breadth ratio) of the solutes, i.e., the more rod-like solutes are retained longer.

PAH isomers of molecular weight 302 were isolated and identified in two Standard Reference Materials: an air particulate extract (SRM 1648) and a coal tar extract that is being certified as SRM 1597. The compounds of interest were isolated from the extracts using normal-phase LC. Thirteen isomers of molecular weight 302 were identified using a combination of GC-MS, reversed-phase LC with fluorescence detection, and Shpol'skii fluorescence spectroscopy of chromatographic fractions collected from the reversed-phase LC analysis. The Shpol'skii fluorescence analysis of the fractions was performed by Prof. Anders Colmsjö of the University of Stockholm. The following isomers were identified in the coal tar extract: dibenzo[a,e]pyrene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene, dibenzo[e,l]pyrene, naphtho[2,1-a]pyrene, naphtho[2,3-a]pyrene, naphtho[2,3-e]pyrene, dibenzo[a,e]fluoranthene, dibenzo[b,k]fluoranthene, naphtho[1,2-k]fluoranthene, naphtho[2,3-b]fluoranthene, naphtho[2,3-k]fluoranthene, and benzo[b]perylene. Most of these isomers have not been identified or quantified previously in either coal tar or air particulate samples. Quantification of these isomers in both the coal tar and air particulate SRM is in progress.

1. G. Grimmer, H. Brune, R. Deutsch-Wenzel, G. Dettbarn, J Misfeld, U. Abel, and J. Timm, **Cancer Letters** 23, 167 (1984).

2. S. A. Wise, B. A. Benner, S. N. Chesler, L. R. Hilpert, C. R. Vogt, and W. E. May, **Anal. Chem.**, in press.

20. Development of a Refined IDMS Method for the Determination of Organic Compounds in CRM Gas Cylinders

S.N. Chesler and F.R. Guenther

A refined isotope dilution/mass spectrometric (IDMS) method for the determination of organics in Certified Reference Material (CRM) gas cylinders has been developed. Previously the CRM cylinders have been analyzed using an external standard, gravimetrically prepared cylinder. This method of quantitation is incapable of detecting a bias in the delivery of the analytes from the cylinder, or in the gravimetric preparation. The IDMS method was designed to overcome these flaws.

The original GC/IDMS method that was developed, employed a cryogenic trap for concentrating large volumes (1-2 liters) of CRM gas prior to cryofocussing onto the head of a capillary GC column. The isotope diluent was added in the form of a solution through a heated injection port. This method provided data with a coefficient of variation of 5 to 10% for the ppb level samples. A large portion of this imprecision can be attributed to uncertainties associated with measurement of the volume of sample taken from the cylinder.

In this approach, a sampling loop of known volume is filled with the gas from a cylinder, with that volume of gas being subsequently injected onto the head of a GC column. A known quantity of a solution containing isotope diluents for each analyte is then injected onto the column and quantitative analysis of the analytes within the gas is then carried out. With knowledge of the loop volume, temperature and pressure, the molar concentration of the analytes within the cylinder can be calculated.

An 8-port valve was configured such that a 3.5 mL stainless steel loop could be filled from the cylinder, and the contents of the loop switched into the gas stream of a capillary column. It was discovered that compounds such as chlorobenzene and bromobenzene concentrate within a loop at room temperature. Therefore, the valve and loop were placed in a thermostated oven and kept at 80° C. A 0.20 mm outside diameter fused silica tube connected the loop to the capillary column through an on-column injector. A regulated flow of 5.5 mL/min was directed through the loop and into the capillary column. At this flow rate, 5 minutes were required to quantitatively transfer the contents of the loop to the column. A head pressure of 20 psi was sufficient to incorporate all of this flow into the capillary column. Approximately 1 m of the capillary column was coiled into a liquid nitrogen bath to cryogenically concentrate and focus the analytes at the head of the column. The loop was purged into the column for 5 minutes at which time 3 μL of an isotope diluent solution was injected through the on-column injector. The GC oven fan was then turned on, the column pressure reduced to 10 psi, and the temperature program started. The liquid nitrogen evaporated quickly after the fan was turned on, and the analytes were then chromatographed. The analytes were detected and quantified using a Hewlett Packard 5970 mass selective detector (MSD). For maximum sensitivity the MSD was used in the selective ion monitoring mode. The response factor solution and the isotope diluent solution were prepared gravimetrically in 100 mL volumetric flasks. Response factors were calculated from multiple injections of the response factor solution.

To validate this approach, a gas cylinder containing a nominal concentration 250 ppb of benzene, toluene, chlorobenzene, and bromobenzene was quantified. Response factors for these components relative to their labeled homologs exhibited a variance of less then 0.5%. The calculated cylinder concentrations had variances of less than 2%. A large portion of this variance is probably associated with uncertainties of injecting small volumes ($\approx$3 μL) of solution onto the column. We are currently contemplating replacing syringe injection with a HPLC type sample valve. Work is continuing to further validate this method, and to compare the results obtained using this approach to those obtained from external standard, gravimetrically prepared cylinders.

21. Refined Analytical Procedure for the Determination of PCBs & Chlorinated Pesticides in Human Liver Samples

S.N. Chesler, R.M. Parris, and S.A. Wise

Thirty individual human liver samples from the Environmental Specimen Bank Facility at NBS have been analyzed for 5 selected polychlorinated biphenyl congeners (PCBs) and 7 chlorinated pesticides using methods developed at NBS. With this procedure, low ng/g levels of these components in human livers can be measured because 1) matrix components that would interfere with the quantitative analysis are removed, 2) analytes are separated into 2 fractions which precludes coelution of some components during the analytical chromatographic analyses, and 3) sample contamination during the analysis is minimized. This project, partially funded by EPA, is part of a continuing effort to archive and characterize several types of environmental samples for future retrospective analyses for both inorganic and organic components.

Concentrations of the PCBs measured ranged from 0.5 to 15 ng/g of wet liver tissue. The individual PCB congeners chosen are among those currently being used by many researchers as marker compounds for the identification and quantification of PCB contamination. 4,4'-DDE levels up to 150 ng/g liver tissue (wet) were measured and concentrations of other pesticides (heptachlor epoxide, transnonachlor, dieldrin, 4,4'-DDD, 2,4'-DDT and 4,4'-DDT) ranged from 0.5 to 25 ng/g liver tissue (wet).

The method developed for these analyses consists of extraction of the sample, two liquid chromatographic cleanup steps, and quantitative analysis using gas chromatography with electron capture detection. To minimize contamination of the sample during the analysis, all glassware is cleaned prior to each use with an RBS-35 surfactant cleaner and a series of solvent washes (acetone, methanol, methylene chloride, and hexane). All glassware and sample solutions are capped with hexane-cleaned aluminum foil except during actual sample transfers. HPLC grade solvents suitable for pesticide residue analyses are used throughout this procedure. These steps are necessary to avoid significant levels of PCB contamination. With each set of samples, an aliquot of a solution containing only the internal standard components was utilized as a system blank and underwent each step of the analyses.

The 30 samples analyzed, which were collected in 1984 in Seattle, Washington, were cryogenically homogenized prior to storage. For analysis, a weighed sample is ground with precleaned anhydrous sodium sulfate to disrupt the cells and remove water from the sample. This mixture is poured into a glass column and 2 mL of internal standard solution is added. Each sodium sulfate mixture is eluted overnight with 2/1 (v/v) hexane/acetone mixture. The volume of the extract is reduced and the percentage extractable fat of each sample is determined. After the volume is further reduced, the sample is filtered using a 0.5 μm glass microfilter. To remove most lipid and other large molecular weight components, the sample is fractionated on a PL-gel preparative scale column. The fraction containing the PCBs and chlorinated pesticides is collected according to previously calibrated retention volumes. The volume of the fraction is reduced and the entire fraction is injected onto a semi-preparative scale aminosilane column from which two fractions are collected. The first fraction contains the PCB components and nonpolar chlorinated pesticides such as hexachlorobenzene while the second fraction contains the more polar chlorinated pesticides (as 4,4'-DDT, dieldrin, transnonachlor and heptachlor epoxide). The fractions are evaporatively concentrated and analyzed using capillary gas chromatography with electron capture detection. The internal standard method of quantification is employed. Each set of samples analyzed included 6 liver samples, duplicate aliquots of 2 liver samples analyzed in the previous set, 1 system blank and 2 aliquots of a gravimetrically prepared calibration solution.

Several liver samples collected in 1982 and previously analyzed for selected chlorinated pesticides are being analyzed this year for individual PCB congeners and reanalyzed for chlorinated pesticides using this method. Also, liver sample aliquots stored at -25 °C, -80 °C and liquid nitrogen vapor temperature will be analyzed for these chlorinated components as part of a study to evaluate the stability of these analytes under various conditions of storage.

22. Specimen Banking Activities for the NOAA National Status and Trends Program

B.J. Koster, W.E. May, M.M. Schantz, S.A. Wise, and R. Zeisler

Since 1979 the Center for Analytical Chemistry, in conjunction with the Environmental Protection Agency, has been involved in an Environmental Specimen Bank Program to evaluate the feasibility of long-term storage of various environmental samples. A pilot banking program was designed to collect several types of environmental accumulators representative of human tissue (liver), marine samples, and food samples. In 1985 the National Oceanic and Atmospheric Administration (NOAA) incorporated specimen banking as part of its National Status and Trends (NS&T) Program. The NS&T Program consists of two monitoring projects, the Benthic Surveillance project and the Mussel Watch project, which are designed to quantify the current status and long-term temporal and spatial trends for key pollutant concentrations and biological indicators of contamination effects in the nation's coastal and estuarine environments. The Benthic Surveillance project consists of 50 U.S. coastal sites at which bottom-feeding fish tissue (muscle and liver) and sediments are collected; whereas the Mussel Watch project consists of 150 sites at which sediment and mussels or oysters are collected. In both of these projects the sediments and tissues are analyzed for the determination of trace elements and various organic pollutants.

Prior to the banking of these marine specimens, detailed protocols were developed, in conjunction with NOAA scientists, for collecting, packaging, and transporting the specimen to the NBS Specimen Bank facility for long-term storage. For the Benthic Surveillance project two duplicate aliquots of 150 g each of fish liver and muscle tissue were obtained from 50-100 fish depending on the size of the species collected. To avoid contamination, fish are necropsied in positive pressure hoods using specially cleaned titanium/teflon tools. Two duplicate aliquots of 150 g each of sediment samples are obtained from each sampling site. These samples are obtained using teflon cylinder corers to remove the top 3 cm of undisturbed surface sediment from three different grabs with a box core sampler. For the Mussel Watch project, duplicate samples of bivalves (50 mussels or 30 oysters) are composited from three stations per sampling site. Duplicate sediment samples, each 150 g composites from three stations per site, are obtained using a teflon coated scoop from the grab sampler. The fish tissue, bivalve, and sediment samples are sealed in teflon bags, frozen, and shipped to NBS for storage at -120 °C. As part of the NS&T specimen banking effort, samples from 12 Benthic Surveillance sites and 30 Mussel Watch sites, collected during the past year, were stored in the NBS Specimen Bank Facility. Samples from a similar number of sites from each project will be added to the bank throughout the NS&T Program. Selected sediment and bivalve samples have been homogenized and analyzed for the determination of both inorganic and organic pollutants. The results of these analyses will be used to provide baseline values for stability evaluation and for comparison with data from other laboratories involved in analyses for the NS&T Program.

Also in support of the NOAA NS&T Program, CAC organized a Quality Assurance Workshop for the various NOAA laboratories and contractors involved in the program. At this workshop the analytical methodologies to be used in the NS&T Program and results from the analysis of NOAA intercalibration samples were discussed in detail. NOAA has requested that NBS organize these workshops on an annual basis as part of the NS&T quality assurance program.

The incorporation of the NOAA specimen banking project into the existing EPA/NBS Environmental Specimen Bank Program provides the necessary support for research and development of banking procedures for marine specimens as originally intended in the pilot program. In addition, the NOAA specimen banking activity provides an excellent model for the role of specimen banking as part of all national biomonitoring programs.

23. Determination of PAH, PCBs, and Chlorinated Pesticides in Marine Tissue and Sediment Samples

S.N. Chesler, M.M. Schantz, and S.A. Wise

As part of NOAA's National Status and Trends (NS&T) Program, surficial sediment, bottom feeding fish, and bivalve molluscs are being collected from a number of sites around the United States yearly. Additional specimens are collected at selected sites for long-term storage in the Environmental Specimen Bank Facility operated by NBS. From those specimens placed in long-term storage, a subset of bivalve tissue and sediment samples has been homogenized for inorganic and organic analysis. These analyses will provide baseline values for the selected sites and will be compared with data from other NOAA laboratories and contractors.

The organic contaminants of interest are polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), and chlorinated pesticides. Methods have been developed in this laboratory utilizing liquid chromatographic fractionation to isolate the three fractions, PAH, PCBs, or more polar pesticides, respectively, from the Soxhlet extracts. In the case of sediment analysis, a silica microfractionation column and an aminosilane liquid chromatographic column are utilized for isolation of the desired fractions; for tissue analysis, a gel permeation column followed by the aminosilane liquid chromatographic column are utilized. The final analyses are done by gas chromatography using the appropriate detector, either flame ionization or electron capture. An internal standard method is used for quantification, and concentrations are reported on a dry weight basis. The liquid chromatographic fractionation method utilized is less time-consuming and requires less exposure of the sample to the atmosphere than conventional column chromatographic fractionation methods.

An intercalibration sediment sample provided by NOAA as part of the Quality Assurance Program for NS&T and six sediment samples from the NS&T Specimen Bank have been analyzed using this methodology. Concentrations of selected PAH in the intercalibration sample range from 0.5 to 3.9 μg/g dry sediment, and those of selected PCBs and chlorinated pesticides range from below the minimum detection limit (< 0.2 ng/g dry sediment) to 127 ng/g dry sediment. These concentrations are in good agreement with values obtained by NOAA's National Marine Fisheries Laboratory using a different clean-up procedure. The six Specimen Bank samples analyzed were collected from the Chesapeake Bay, MD; Mississippi River Delta, LA; Corpus Christi, TX; Dana Point, CA; Nisqually Beach, WA; and Elliott Bay, WA. For these sediment samples, PAH concentrations ranged from below the minimum detection limit (<0.02 μg/g dry sediment) to 5.3 μg/g dry sediment while the PCB and chlorinated pesticide concentrations ranged from below the minimum detection limit to 58 ng/g dry sediment.

An intercalibration mussel sample and six bivalve samples stored in the NS&T Specimen Bank have been homogenized and will be analyzed this year. The bivalve samples were collected from San Diego, CA; Galveston Bay, TX; Fort Johnson, SC; Dorchester Bay, MA; Pascagoula Bay, FL; and Baltimore Harbor, MD. In the future, additional sediment and bivalve samples will be analyzed as well as fish liver and possibly fish tissue samples.

24. Reference Laboratory Activities Associated with the National Cancer Institute Cancer Chemoprevention Programs

W.E. May, R.C. Paule, and R. Schaffer

For the past two years the Center for Analytical Chemistry has been operating a quality assurance program for laboratories that measure serum and plasma concentrations of ascorbic acid (vitamin C), beta-carotene, retinol (vitamin A), selenium, alpha-tocopherol (vitamin E), and zinc. The Division of Cancer Prevention and Control of the National Cancer Institute (NCI) asked NBS to organize the program in order to ensure the long-term reliability of measurements being made in conjunction with several NCI-supported investigations of the possible cancer-prevention benefits of these micronutrients in populations of humans at high risk for certain forms of cancer. In addition to the NCI-sponsored laboratories, other laboratories that analyze for these substances for other medical reasons were invited to join the program; this allowed us to have results from 10 to 20 laboratories per analyte. The serum concentrations of these nutrients are typically below 1 mg/L for beta-carotene, retinol, and selenium; about 1 mg/L for zinc; and about 10 mg/L for ascorbic acid and alpha-tocopherol. Each laboratory used methods that they routinely employ for analysis of the round-robin samples.

For the organic micronutrients, almost all laboratories use high-performance liquid chromatography (HPLC) with UV-visible detection, but methodologic details vary among the laboratories. Their methods differed also from those of NBS. For ascorbic acid, we use ion-exchange HPLC with isocratic elution and UV-VIS and electrochemical detection. For the fat-soluble vitamins, we use C-18 reverse-phase HPLC with gradient elution and both wavelength-programmed UV and electrochemical detection.

For selenium, the various laboratories use four different atomic absorption methods and an isotope dilution mass spectrometric method. Two atomic absorption methods are being used for zinc. We use atomic absorption methods for both analytes.

Overall laboratory proficiency for these analyses is shown from our statistical analysis on the most recently obtained interlaboratory test results. After removing outliers, the NBS and the laboratory grand means for individual samples were generally within 5%. The values calculated for the percent coefficient of variation of a single measurement made by a single laboratory ranged from 12-28% for the organics, 17-27% for selenium, and 7-12% for zinc. (This coefficient of variation equals 100 $S_x/\bar{x}$ where $\bar{x}$ is the grand mean and S_x is the square root of the sum of the within and between components of variance.) These relative imprecision values are large partly because of our practice of retaining as much laboratory data as possible for statistical analysis. In general, a result had to be more than 60% lower or 100% higher than the grand mean of all laboratory measurements to be excluded as an outlier. Even with these wide selection limits and depending on the analyte, we classified from zero to 20% of laboratory results for the different samples as outliers.

We are also serving as a reference laboratory for a collaborative epidemiologic research study being carried out by the Epidemiology and Biostatistics Program of the National Cancer Institute for evaluating the effects of ionizing radiation on cancer risk among atomic bomb survivors in Hiroshima and Nagasaki. One component of the study involves determinations of serum nutrient levels (beta-carotene, retinol, selenium, alpha-tocopherol, and zinc) in persons exposed to high or low doses of radiation, who had donated blood in the 1970's and subsequently developed cancer. The serum from approximately 600 donors is to be assayed in two laboratories in Japan, one for the metals, another for the vitamins. We are to determine both the vitamins and metals in split samples from a random selection of the donor sera.

To obtain preliminary information concerning the quality of the data that might be forthcoming, the Japanese laboratories were sent samples that had been analyzed previously by NBS and other U.S. NCI laboratories. Results have been received thus far only for the vitamins. From the biases in these results and a description of the methodology employed, we recognized that the Japanese laboratory was using a vitamin analysis method which our recent investigation has been shown to be subject to non-reproducible 40-50% biases. This method was published by one of the laboratories in our quality assurance program. After consulting with NBS personnel the source of error was discovered, and its use has been abandoned in that laboratory. The negative information on that method is now being submitted for publication.

We have been informed that neutron activation analysis will be used for the metal analyses run in Japan. Both NBS and the Japanese laboratory responsible for metals analyses are analyzing a pooled serum sample by atomic absorption spectroscopy and neutron activation analysis, and (with the cooperation of a USDA lab) also getting results by isotope dilution mass spectrometry, to ensure that results for the metals are not method/technique specific.

25. International Round Robin Study on the Determination of PAH and Nitro-PAH in Environmental Samples

B.A. Benner, L.R. Hilpert, W.A. MacCrehan, W.E. May, and S.A. Wise

Development of new analytical techniques and the refinement of established techniques continues at a rapid pace in analytical laboratories throughout the world. A challenging problem in analytical chemistry is the accurate determination of individual organic species in complex mixtures such as diesel and air particulate extracts. An effective means to gauge the variability among the diverse analytical techniques used is through interlaboratory comparisons of analyses of complex mixtures.

During the past year, we have conducted an international interlaboratory comparison study, sponsored in part by the Coordinating Research Council and the Department of Energy, on the determination of PAH and nitro-PAH in three complex environmental samples: a diesel particulate extract, an urban air particulate extract, and a solid diesel particulate sample. The air particulate and diesel particulate extracts were obtained from SRMs 1648 and 1650, respectively. Samples were distributed throughout the world to laboratories involved in the measurement of PAH and nitro-PAH. The laboratories were requested to use analytical techniques of their choice to determine PAH and nitro-PAH. Laboratories were asked to determine only those compounds which they routinely measure so that a realistic assessment of the state-of-the-art for environmental analysis might be obtained. However, all laboratories were asked to measure a core set of compounds consisting of phenanthrene, fluoranthene, benz[a]anthracene, benzo[a]pyrene, benzo[ghi]perylene, and 1-nitropyrene. The selection of this core group of compounds was necessary to ensure that we obtained sufficient data on a minimum number of analytes to form a valid data base for statistical comparison.

Data were received from 29 laboratories including NBS. The participating laboratories were from the following countries: the United States (12), Europe (Sweden, Norway, Germany, France, and Italy) (9), Japan (5), Canada (2), and Australia (1). These laboratories used the following analytical techniques for the PAH measurements: reverse-phase liquid chromatography with fluorescence detection (10 labs), liquid chromatography with diode array UV detection [1 lab], capillary gas chromatography (GC) [10 labs], Gas chromatography-mass spectrometry (GC-MS) [9 labs], thin-layer chromatography (TLC) [2 labs], and direct fluorescence measurements without chromatographic separations [2 labs]. At NBS we used two techniques for the determination of the PAHs: [1] reverse-phase LC with fluorescence detection and [2] GC-MS. Three techniques were used at NBS for the determination of nitro-PAH: [1] reverse-phase LC with fluorescence detection after on-line reduction of the nitro-PAH to the corresponding amino PAH, [2] GC-MS, and [3] reverse-phase LC with reductive electrochemical detection. The other participating laboratories used similar LC and GC-MS techniques for their nitro-PAH determinations.

The evaluation of the data from all of the laboratories is in progress to assess the state of the art for these determinations. In addition, this study will provide information on differences among the various analytical techniques used routinely for making these measurements.

26. Construction of a New Sample Preparation Laboratory

S.N. Chesler and R.M. Parris

A new Sample Preparation Laboratory has been constructed in Modules B105-107 of the Chemistry Building. This facility replaces the non-functional and outmoded walk-in coldroom and an area used by the Mass Spectrometry Group. The old sample preparation area A-106 will now be used as a general purpose laboratory by the Mass Spectrometry Group.

The new laboratory was designed to accommodate three operations: glassware cleaning and storage, sample storage, and sample preparation. Since the laboratory will be used for general trace organic analysis, special care was taken in choosing the laboratory accouterments. The flooring is a continuously welded polyvinyl chloride material which is solvent resistant and nonporous so that any spills can be completely removed by solvent washing. The bench tops are made from a solid epoxy-resin substance and is non-contaminating and nonporous. The walls and ceiling are coated with a highly reflective epoxy based paint which, like the floor, can be easily decontaminated. Two all-stainless steel fume hoods are also provided as vented work areas.

The laboratory is equipped with a 7 cubic foot forced air oven that can operate above 500 °C. At these temperatures all measurable organic contaminants are removed by oxidation and/or vaporization. We have shown that no traces of PCBs (< 50 pg/g) remain on glassware that had been contaminated with Aroclor 1260 just prior to the thermal cleaning operation. Prior to the thermal cleaning, all glassware will be detergent washed and rinsed with distilled water to avoid obvious contamination to the oven interior. The heating cycle is 22 hours with an 18-hour thermal soak at 500 °C.

The laboratory has a total of 75 cubic feet of low-temperature sample storage, although long-term storage of samples in the laboratory is not contemplated. This includes a 4 °C refrigerator, two -20 °C freezers and a -76 °C ultracold freezer. These storage areas are also used to keep small amounts of chemical standards and solutions currently in use. All the cold storage is alarmed such that appropriate personnel are alerted in case of a refrigeration failure.

The central bench area of the new laboratory has space for 14 Soxhlet extractors and three preparative single pump liquid chromatographs. In this area initial extraction and then extract purification takes place. Six additional Soxhlet extractors can be placed in the fume hood for use with very toxic extractants or samples, such as benzene or diesel particulate material. Benchspace on the sides of the laboratory is provided for a rotary evaporator, laboratory centrifuge, a large-scale Soxhlet extractor, a ultrasonic bath and various stirrers and agitators. A stone weighing table in the corner of the laboratory provides a location for an analytical micro-balance and a high-capacity balance. A special records-keeping area is located in an alcove above which shelf space is available for storage of reference texts, laboratory notebooks, etc. A large, high-capacity shelf is located above the refrigerated storage area and will be used to store sampling equipment, high-capacity metallic containers and shipping materials.

C. Outputs and Interactions
(Organic Analytical Research Division)

1. Publications

Byrd, G. D., Fatiadi, A. J., Simons, D. S., and White V, E., Laser Desorption Mass Spectrometry of Squaric Acid and its Salts, Org. Mass Spectrom. 21, 63-68 (1985).

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Cohen, A., Hertz, H. S., Schaffer, R., Welch, M. J., and White V, E., Synthesis of 2-Amino-1,5-Dihydro-1-(Methyl-^{13}C)-4H-Imidazol-4-One-5-^{13}C (Creatinine-$1^{3}C_{2}$), Journal of Labelled Compound Radiopharmacology, in press.

Coxon, B., Complete Assignment of the ^{13}C NMR Spectra of the Ring Forms of Digitoxose by DEPT Spectrum Editing and Two-Dimensional CH Chemical Shift Correlation Spectroscopy, in press.

Coxon, B., Optical Rotation, Physico-Chemical Properties (IUPAC), in press.

Domalski, E. S., Churney, K. L., Ledford, Jr., A. E., Bruce, S. S., Buckley, T. J., Parris, R. M., and Chesler, S. N., Monitoring the Fate of Chlorine from MSW Sampling through Combustion, Proceedings of EPRI Municipal Solid Waste as a Utility Fuel Seminar (Nov. 20-22, 1985, Madison, Wisconsin), in press.

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Espinosa-Leniz, R. and White V, E., Silver Sulfonates: A Novel Calibration Material for Field Desorption Mass Spectrometry, Biomedical Mass Spectroscopy, in press.

Foley, J. P. and May, W. E., Optimization of Secondary Chemical Equilibria in Liquid Chromatography (SCE-LC): Variables Influencing the Self-Selectivity, Retention, and Efficiency in Acid-Base Systems, Anal. Chem., in press.

Foley, J. P. and May, W. E., Optimization of Secondary Chemical Equilibria in Liquid Chromatography: Theory and Verification, Anal. Chem., in press.

Guenther, F. R., Chesler, S. N., and Parris, R. M., Analysis of Nitrogen Heterocycles in Shale Oil by a Dual Capillary Column Heart Cutting Technique, J. Chromatogr., in press.

MacCrehan, W. A. and Brown-Thomas, Determination of Phenols in Petroleum Crude Oils Using LCEC, Anal. Chem., in press.

Margolis, S. A. and Black, I., The Stabilization of Ascorbic Acid and Its Measurement in Non-fat Dry Milk, J. Offic. Anal. Chem., in press.

Margolis, S. A. and Coxon, B. C., Identification and Quantitation of the Impurities in Sodium Pyruvate, Anal. Chem., in press.

May, W. E., Schaffer, R., and Paule, R. C., Establishment of a Quality Assurance Program for the National Cancer Institute's Chemioprevention Program, Journal of the Cancer Institute, in press.

Reeder, D. J., Development of Standards for Electrophoresis and Electrofocusing, ACS Symposium Series: *New Directions in Electrophoretic Methods*, Jorgenson, J. and Phillips, M. (Eds.), in press.

Reeder, D. J., Hancock, D. K., Edwards, J. J., and Richie, K. L., Electrophoresis Society Meeting Hosted at NBS, NBS J. Res. (Conf. Report), in press.

Schantz, M. M. and Chesler, S. N., A Supercritical Extraction Procedure for the Removal of Trace Organic Species From Solid Samples, J. Chromatogr., in press.

Syty, A., Christensen, R. G., and Rains, T. C., Trace Determination of Cr (III) and Cr (VI) by LC/AAS with On-Line Preconcentration, *Atomic Spectroscopy*, in press.

Wise, S. A., Benner, B. A., Chesler, S. N., Hilpert, L. R., May, W. E., and Vogt, C. R., Characterization of the Polycyclic Aromatic Hydrocarbons from Two Standard Reference Material Air Particulate Sample, Analytical Chemistry, in press.

Yap, W. T. and Durst, R. A., A Finite Elements Digital Simulation of Chronoamperometry with Polymer-Modified Electrodes, J. Electronal. Chem., in press.

Byrd, G. D., Richie, K. L., Sniegoski, L. T., and White V, E. Direct Calibration of GC/MS Systems Using SRM Gas Cylinders, NBSIR, in press.

Chesler, S. N., Rebbert, R. E., and Enagonio, D. P., Examination of the AAMI ETO Residues Recommended Practice and a Determination of ETO Kinetics in Water, Report to FDA, in press.

2. *Talks*

W. E. May, "Analytical Methods and Standards for the Determination of Trace Organic Species in Complex Mixtures," Department of Chemistry, South Carolina State University, Orangeburg, SC, October 14, 1985. *Invited*

L. R. Hilpert, "The Analytical Methods for the Certification of a Diesel Particulate SRM," Coordinating Research Council, CAPE-30 Project Meeting, University of Nebraska, Lincoln, NE, October 15, 1985. *Invited*

W. E. May, "Standard Reference Materials and their Uses in the Determination of PAH and Related Compounds in Complex Mixtures," Tenth Anniversary of the Internatinal Symposium on Polynuclear Aromatic Hydrocarbons," Columbus, OH, October 21, 1985.

B. Coxon, "Software for Two-Dimensional NMR Spectrum Editing," Bruker NMR Users' Conference, Nashua, NH, October 30, 1985.

B. Coxon, "Two-Dimensional NMR spectrum Editing of Carbohydrates," Department of Pharmacology and Experimental Therapeutics, The Johns Hopkins University School of Medicine, Baltimore, MD, November 8, 1985.

S. A. Wise, "The Environmental Specimen Bank Program at NBS," Belgian Embassy, Washington, DC, November 8, 1985. Invited

P. Ellerbe, "Six-Month Progress Report on the Activities of the CAP Research Associate," College of American Pathologists; Standards Committee, Scottsdale, AZ, January 14, 1986. Invited

B. Coxon, "One-and Two-Dimensional NMR Spectrum Editing," Department of Chemistry, American University, Washington, DC, February 7, 1986.

A. L. Plant, "Collisional Quenching of Zanthene Dyes Applied to Study the Mechanisms of Complement-Mediated Lysis of Lipid Vesicles," Biophysical Society, 30th Annual Meeting, Brooks Hall, San Francisco, CA, February 10, 1986.

S. A. Wise, "Selectivity in Reversed-Phase Liquid Chromatography," Analytical Chemistry Division Seminar, The Pennsylvania State University, State College, PA, Feb. 14, 1986. Invited

W. A. MacCrehan, "Liquid Chromatography with Electrochemical Detection," Food and Drug Administration, Washington, DC, February 28, 1986. Invited

D. J. Reeder, "Electrophoresis in an Analytical Laboratory Setting," Chemistry Department, University of Maryland, College Park, MD, February 28, 1986. Invited

W. A. MacCrehan and E. Schonberger, "Detection of Retinol and Its Impurities Using LC/UV, EC," Pittsburgh Conference, Atlantic City, NJ, March 12, 1986.

W. A. MacCrehan and E. Schonberger, "Determination of Fat Soluble Vitamins in Serum Using LCEC," Pittsburgh Conference, Atlantic City, NJ, March 12, 1986.

G. D. Byrd, "Calibration of GC/MS Instrumentation for the Analysis of Volatile Organics Using Cryogenic Trapping," Pittsburgh Conference, Atlantic City, NJ, March 12, 1986.

K. L. Richie, "Results of an Interlaboratory Round Robin Using Isoelectric Focusing to Assess Reproducibility of Rehydratable," 1986 Meeting of the American Branch of the Electrophoresis Society, Holiday Inn, Gaithersburg, MD, March 26, 1986.

R. Schaffer, "NBS Definitive Method for Cholesterol," Laboratory Standardization, National Cholesterol Education Program, National Heart, Lung and Blood Institute, National Institutes of Health, Bethesda, MD, April 7, 1986. Invited

R. G. Christensen, "Preconcentration and Determination of Trace Cr(VI) by LC/AAS," Chromexpo-1986, Rockville, MD, April 10, 1986.

S. A. Wise, "The Need for Environmental Specimen Banking," Commission on Life Sciences, Board on Environmental Studies and Toxicology, Committee on Biological Markers, National Academy of Science, Washington, DC, May 8, 1986. Invited

F. R. Guenther, "The Determinatin of Individual Organic Compounds in Complex Mixtures," Seventh International Symposium on Capillary Chromatography," Nagara, Gifu, Japan, May 11, 1986.

J. Brown-Thomas, "Liquid Chromatography," Montgomery Public School's Science Conference, Wooton High School, Rockville, MD, May 17, 1986. Invited

S. A. Wise, "Determination of Dibenzopyrenes and Dibenzofluoranthenes by Liquid Chromatography," Tenth International Symposium on Column Liquid Chromatography, San Francisco, CA, May 18-23, 1986.

L. C. Sander, "Characterization of Bonded Phase Sorbents by Small-Angle Neutron Scattering," Tenth International Symposium on Column Liquid Chromatography, San Francisco, CA, May 18-23, 1986.

L. R. Hilpert, "Determination of PAH and Alkylated-PAH in Particulate Extracts Using Negative Ion Chemical Ionization Mass Spectrometry," 34th Annual Conference on Mass Spectrometry and Allied Topics, Hyatt Regency, Cincinnati, OH, June 10, 1986.

M. J. Welch, "Photodissociation of Negative Ions Generated by LSIM," 34th Annual Conference on Mass Spectrometry and Allied Topics, Hyatt Regency, Cincinnati, OH, June 10, 1986.

P. Ellerbe, "Development of a New Definitive Method for Uric Acid," 34th Annual Conference on Mass Spectrometry and Allied Topics, Hyatt Regency, Cincinnati, OH, June 10, 1986.

W. A. MacCrehan and E. Schonberger, "Determination of Fat Soluble Vitamins in Serum Using LC with Absorbance and Electrochemical Detection," Electroanalysis na hEireann, Dublin, Ireland, June 10, 1986.

S. Meiselman, "Isotope Dilution Mass Spectrometry Utilizing Electric Deflection Plate Switching," 34th Annual Conference, American Society for Mass Spectrometry, Hyatt Regency Hotel, Cincinnati, OH, June 10, 1986.

G. D. Byrd, "Development of a Confirmatory Test for Exposure to 3-Quinuclidinyl Benzilate (BZ)," 34th Annual Conference on Mass Spectrometry and Allied Topics, Hyatt Regency Hotel, Cincinnati, OH, June 12, 1986.

W. A. MacCrehan and S. D. Yang, "A Catalytic Oxygen Scrubber Column for the Reductive LCEC of Nitro-PAH in Diesel Soot," Electroanalysis na hEireann, Dublin, Ireland, June 12, 1986.

W. E. May, "Establishment of Interlaboratory Comparability for Trace Organic Environmental Measurements," 2nd Annual DOE Contractors Meeting on Health & Environmental Effects of Complex Chemical Mixtures," Lake Lawn Lodge, Delavan, WI, June 17, 1986. Invited

B. A. Benner, "Mobile Sources of Polycyclic Aromatic Hydrocarbons (PAH) and Nitro-PAH: A Roadway Tunnel Study," Fifth Symposium on Environmental Analytical Chemistry: Atmospheric Chemistry and Source Apportionment, Provo, UT, June 18-20, 1986.

S. A. Margolis and B. Primack, "The Alkaline Rearrangement of NADP and the Isolation of an Inhibitor of Oxidation and Reduction of NADP(H) by

Secondary Alcohol Dehydrogenase," Gordon Conference on Enzymes and Coenzymes, Kimball Academy, Merraden, NH, July 30, 1986.

B. Coxon, "2D J(CH)-Resolved^{13} NMR Spectrum Editing of Carbohydrates," XIII The International Carbohydrate Symposium, Cornell University, Ithaca, NY, August 8, 1986.

S. A. Wise, "Determination of Dibenzopyrenes and Dibenzofluoranthenes by Liquid Chromatography," ARCO Chemical Company, Newtown Square, PA, August 25, 1986. Invited

L. T. Sniegoski, "Development of a Confirmatory Chemical Test for Exposure to 3-Quinyclidinyl Benzilate (BZ)," 20th Middle Atlantic Regional Meeting, September 2-4, 1986.

D. J. Reeder, "A Chemometric Approach to Analysis of Protein Patterns from Ultra-Thesis Isoelectric Focusing Gels," Fifth International Meeting of The Electrophoresis Society, Conference Centre, Royal Borough of Kensington and Chelsea Town Hall, London, England, September 11, 1986.

D. Shea and W. A. MacCrehan, "Role of Biogenic Thiols on the Solubility of Sulfide Minerals," American Chemical Society Meeting, Anehiem, CA, September 12, 1986.

3. Committee Assignments

Willie E. May
- Chairman, Center for Analytical Chemistry Analytical Workshop Committee
- Member, ASTM Committee D19 on Water; Committee E19 on Chromatography
- Member, ACS Environmental Chemistry Division
- Board of Directors, Washington Chromatography Discussion Group
- Member, Coordinating Research Council-Air Pollution Research Advisory Board
- Member, ICPAH Research Steering Committee
- Board of Governers, International PAH Symposium
- Member, NIH Minority Biomedical Instrumentation Review Board
- Member, Food Irradiation Research Steering Committee

Bruce Coxon
- Member, Committee E13 on Molecular Spectroscopy
- Secretary, ASTM Committee E13.07 on Nuclear Magnetic Resonance,
- Member, Program Committee 12th International Carbohydrate Symposium
- Member, Program Committee 27th Experimental NMR Conference

Richard A. Durst
- Member, ASTM Committee D19 on Water
- Member, Board of Advisory Editors, Ion-Selective Electrode Reviews
- Member, IUPAC Committee V on Analytical Chemistry; Subcommittee 5 on Electroanalytical Chemistry
- Member, NCCLS Subcommittee on Electroanalytical Methods; Subcommittee on pH and Blood Gases
- Member, NBS Research Advisory Committee

Jesse J. Edwards
- Member, ASTM Committee E48 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

Laurence R. Hilpert
- Member, ASTM Committee D34 on Waste Disposal
- Member, ASMS Environmental Committee

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

Robert Schaffer
- Member, NCCLS Area Committee for Clinical Chemistry
- Member, NCCLS Area Committee on Evaluation Protocols
  - Subcommittee on Creatinine
  - Subcommittee on Theophylline
- Member, Council for National Reference System in Clinical Chemistry
- Delegate, Laboratory Standardization Panel of the National Cholesterol Education Program

Michael J. Welch
- Member, Standards Committee of the Americal Association of Clinical Chemistry

Stephen A. Wise
- Program Chairman, Washington Chromatography Discussion Group

4. Other

a. Seminars

September 13, 1985 - Prof. Jarmila Janatova, University of Utah, "Biochemistry of Complement." (Division Sponsor: R. A Durst)

January 7, 1986 - Barry Lavine, Pennsylvania State University, "Pattern Recognition Studies of Complex Chromatographic Data Matrices: Taxonomy Based on Chemical Constitution." (Division Sponsor: S. A. Wise)

February 3, 1986 - Carl Marrese, Bacharach Instruments, "Electrocatalysis at Chemically-Modified Electrodes and Diffusion in BSA Gel Coated Electrodes." (Division Sponsor: D. J. Reeder)

March 17, 1986 - Harlan K. Jones, University of Utah, "Field Flow Fractionation of Colloidal Particles." (Division Sponsor: S. A. Wise)

March 19, 1986 - Grace Picciolo, Food & Drug Administration, "Chemical Biosensors as Medical Devices." (Division Sponsor: R. A. Durst)

April 16, 1986 - Deborah Winn, National Center for Health Statistics, "Analytical Measurements and Quality Assurance Needs for National Health and Nutrition Evaluation Survey (NHANES-III)." (Division Sponsor: W. E. May)

May 8, 1986 - Louis E. Henderson, NCI-Frederick Cancer Research Facility, "Separation of Proteins by Reversed Phase HPLC." (Division Sponsor: D. J. Reeder)

May 14, 1986 - Maurice Verzele, State University of Ghent, Ghent, Belgium, "Recent Advances in Liquid Chromatographic Packing Materials." (Division Sponsor: S. A. Wise)

May 28, 1986 - Beverly Packard, Johns Hopkins University, "Probing Cellular Dynamics with Fluorescence Spectroscopy." (Division Sponsor: A. Plant)

June 24, 1986 - Neal Craft, USDA, "Analysis of Vitamins in Serum." (Division Sponsor: R. Schaffer)

July 7, 1986 - Joe P. Foley, Louisiana State University, "Systematic Errors in Chromatographic Analyses." (Division Sponsor: W. E. May)

July 11, 1986 - Anders Colmsjö, University of Stockholm, Stockholm, Sweden, "Liquid Chromatography and Low-Temperature Fluorescence for the Determination of Organic Compounds." (Division Sponsor: S. A. Wise)

July 23, 1986 - Marcel Gonzalez, University of Pennsylvania, Philadelphia, PA, "Role of the Carboxylate in Yeast Inorganic Pyrophosphatase." (Division Sponsor: D. J. Reeder)

August 12, 1986 - Donald Atha, Beth Israel Hospital, Boston, MA "Structure/Function of Heparin Binding to Antithrombin." (Division Sponsor: D. J. Reeder)

August 19, 1986 - Andrew Alpert, Columbia, MD, "Covalent Coatings on Silica for Chromatography and Immobilization of Proteins and Peptides." (Division Sponsor: A. L. Plant)

August 25, 1986 - Rebecca A. Cowling, "Chemical Modification of Dihydropyrimidine Amidohydrolase." (Division Sponsor: D. J. Reeder)

August 29, 1986 - Winfred Malone, NCI, "Analytical Needs to Support NCI Cancer Chemo-Prevention Programs." (Division Sponsor: W. E. May)

b. Conferences Sponsored

December 5&6, 1985 - W. E. May, NOAA/NBS Methods Development/Quality Assurance Workshop

March 26-28, 1986 - D. J. Reeder, Electrophoresis Society Meeting

May 28-29, 1986 - W. E. May and R. Schaffer, 2nd NBS/NCI Micronutrient Analysis Q.A. Workshop

c. SRM Activities

SRM 17D,	Sucrose
SRM 41C,	D-Glucose (Dextrose)
SRM 911B,	Cholesterol
SRM 914A,	Creatinine
SRM 927a,	Bovine Serum Albumin
SRM 1549,	Non-Fat Dry Milk
SRM 1563,	Cholesterol and Fat Soluble Vitamins in Coconut Oil
SRM 1585,	Chlorinated Biphenyls in 2,2,4-Trimethylpentane (Isooctane)
SRM 1587,	NPAH in Methanol
SRM 1588,	Organics in Cod Liver Oil
SRM 1596,	Dinitropyrenes in Methylene Chloride
SRM 1597,	Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar
SRM 1648,	Urban Particulate Matter
SRM 1649,	Urban Dust/Organics
SRM 1650,	Diesel Particulate Material
SRM 1829,	Alcohols in Reference Fuel
SRM 1837,	Methanol (9 volume percent) and t-Butanol (6 volume percent) in Reference Fuel
SRM 1838,	Ethanol (10 volume percent) in Reference Fuel
SRM 1839,	Methanol (0.3 volume percent) in Reference Fuel
SRM 1916A,	Bilirubin

IV. Gas and Particulate Science Division

Harry L. Rook, Chief
William D. Dorko, Deputy Chief

A. Division Overview

The Gas and Particulate Science Division conducts research to develop new and improved techniques for the preparation and analysis of gases and microscopic regions of matter. These include research leading to (a) improved measurements of gaseous species in the atmosphere and in specially prepared gas mixtures, (b) new or improved methods of laser spectrometry for the analysis of specific gaseous molecules, (c) new chemometric techniques for improved chemical measurements, (d) improved quantitative x-ray fluorescence analysis, (e) improved analytical methods for quantitative electron, ion, and photon microanalysis, and (f) the preparation and certification of standards for measurement quality assurance in analytical chemistry. The Division responds to the measurement and standards needs of other Federal agencies, industrial organizations, universities, and governments, both state and local. The research efforts are conducted by the five groups which comprise the Division and are divided about equally between the two general areas of gas analytical chemistry and microanalytical chemistry.

During the past year, research in gas measurement has been directed toward developing new methods for trace and ultra-trace gas analysis and standards and toward improving the accuracy of data produced by existing methodologies and used in the certification of NBS SRMs. Research in gas analysis is carried out in the Gas Metrology, Atmospheric Chemistry, and Laser Analytical Spectrometry Groups of the Division. Their research plans and results are coordinated in quarterly Group Leaders meetings devoted to research planning. Selected highlights in gas measurement research follow.

Research in laser spectrometry continued to improve quantitative spectroscopic measurements by both investigating better calibration techniques and also by investigating potential problems inherent in the spectrometry itself. Better calibration techniques were used for the quantitation of absorption and pressure-broadening coefficients for NO_2, which is an atmospheric gas of interest to a variety of agencies and industries. Traditionally, the determination of these coefficients has been accomplished by using measured pressures of pure NO_2 in an absorption cell as the calibrant. Systematically low absorption coefficients are likely to result because of the loss of NO_2, due to its reactive nature, and also because of the equilibrium between NO_2 and N_2O_4. These problems were eliminated by utilizing dynamically generated dilute NO_2 standards employing permeation tubes which were specially prepared in-house. The diluted standards eliminated the N_2O_4 as a molecular species and the continual flushing of the cell, due to the dynamic nature of the calibrant, eliminated the reactive losses due to wall contact. The concentration of the NO_2 in the calibration gas was determined by gravimetrically determining the weight loss of the permeation tubes, by Fourier transform infrared spectroscopy and by gas phase titration (in which O_3, NO and NO_2 were measured). Using this approach, with the redundant verification of the calibration concentration, absorption and pressure-broadening coefficients for over 26 different vibration-rotation lines of NO_2 in one of the most important spectral regions of the infrared (the ν_3 band at 6.2 μm) were determined.

Significant progress has also been made in improving the photometric accuracy of TDLAS measurements. Employing techniques, line fitting algorithms and system improvements discussed in last year's report, a subtle, systematic source of error has been identified. For quantitative purposes, many investigators correct determinations based upon peak absorbance measurements using the increased absorption linewidth as a scaling factor. This is accurate as long as all of the causes of increased linewidth are recognized and included. Our investigations have recently revealed a heretofore unreported source of increased linewidth and this is from laser frequency jitter caused by mechanical shocks from the closed-cycle refrigerator compressor. To eliminate this problem, a microprobe-triggering circuit has been completed which tracks the motion of compressor piston and allows data to be taken only during the central portion of the cycle.

Another atmospherically active and important molecule was also studied. The stoichiometry of the gas phase titration reaction between NO and O_3 to produce NO_2 was reinvestigated using improved techniques for the generation and analysis of the three components of interest. The results suggest that the presently accepted value for the O_3 absorption cross-section at 254 nm should be lowered by 1 to 1.5% which is in agreement with results recently obtained by university researchers employing a completely different technique.

Major accomplishments have continued in developing and evaluating compressed gas standards with the analytes of interest in the low concentration range. The analytes have ranged from toxic organic compounds to inorganic gases which are precursors to acid rain. The gas cylinder mixture of 17 volatile toxic organic components, all at about 10 ppb, which was prepared last year has been used by EPA/EMSL/RTP for calibrating GC/MS measurements of air samples obtained from an accidental chemical emission in the vicinity of a major urban area. The cylinder was returned to NBS after several months and subsequent reanalysis has shown that the contents have remained stable. This is quite important, since this is the first time that a gas mixture, this complex, and with components at such trace concentration levels has been verified to be well characterized and stable. The other area of trace level gas standards is for dry acid deposition measurements. Specially prepared mixtures of both SO_2 in Air and NO in N_2 at the 100 ppb level have been evaluated over a period of time and have shown excellent stability. A dynamic dilution system to provide a 100 to 1 dilution has also been developed so that these mixtures can be accurately diluted to provide standards at 1 ppb, which is the level of analytical significance.

Other areas of activity include (1) an extensive evaluation of the errors associated with the gravimetric procedure used for the development of high accuracy gaseous SRMs of carbon dioxide in air (300 to 400 ppm) for the global monitoring of temporal changes in atmospheric carbon dioxide levels, (2) the quantitative determination of the strengths of infrared absorption bands of halocarbons F-11 and F-12 at stratospherically-relevant temperatures, (3) initiation of the development of multicomponent gas standards for automotive emission testing for EPA and State Inspection/Monitoring programs, and (4) the analytical certification to restock 50-cylinder batches of about 20 gaseous SRMs.

Chemometrics is a new area of research for the Division. A major Competence Building proposal was developed this year and presented to the NBS Director. This proposal will also be the planning guide for research during the next five years, with the level of effort determined by funding and staff which we can hire or commit to this area. Chemometrics employs advanced mathematical statistical methods together with expert chemical knowledge for the design and evaluation of complex, multicomponent chemical measurement processes. Recent activities have emphasized detection limits, quality assurance, multivariate analysis, and planning for an integrated chemometric approach to the chemical measurement process. Fundamental and applied aspects of the limit of detection in analytical chemistry was the subject of a two day symposium organized by the group leader for the spring 1986 national meeting of the ACS.

Source apportionment of bulk atmospheric, carbonaceous particles and gases has continued to be another major activity. The work, with collaboration with groups within and outside the U.S., has focused on basic advances in the measurement of natural levels of ^{14}C in trace levels of atmospheric carbon. A microsample preparation system developed at NBS has made it possible to prepare excellent targets for accelerator mass spectrometry (AMS) with less than 100 μg carbon in the original atmospheric sample. These ^{14}C measurements have been used to discriminate CO and particles from woodburning and fossil fuel combustion, and also to estimate source contributions for polycyclic aromatic hydrocarbons for the EPA's Integrated Air Cancer Program.

The basic mission of microanalysis research is to advance the development and application of microbeam analysis techniques for the chemical, morphological, and crystallographic characterization of matter in the micrometer and submicrometer spatial scales. Compositional mapping has continued to be a major theme for much of the work. A new method has been developed which makes direct use of a spectrometer wavelength scan across a peak to provide the basis for mathematically constructing a "standard map" for subsequent calculation of the k-value map for the unknown. This procedure results in significant benefits by eliminating the time required for acquiring the standard maps and by improving the statistical quality of the data for the standard. The new procedure should make compositional mapping more readily applicable to practical problems.

In the area of mass spectrometry microanalysis, the automatic measurement of isotopic ratios of arrays of discrete particles viewed in the ion microscope, a form of secondary ion mass spectrometry, has been accomplished. The image processing software operates in digital images recorded by a TV camera which views the fluorescent screen of the ion microscope. The computer image processor automatically recognizes particles, corrects for background, and calculates isotopic ratios from a series of images taken at various masses.

Special efforts have been concentrated in the area of laser Raman microanalysis (LRM) as applied to biological problems. LRM represents one of the most promising molecular microanalysis techniques for use in the area of biotechnology.

Research in x-ray fluorescence continues to focus on ways to improve accuracy and sensitivity these measurements. A major accomplishment has been the determination of the effects of different sources of mass absorption coefficients in fundamental parameter computer programs on the results of analysis. When coefficients from three commonly used compilations are used, differences of 10% or greater are often found in the results for elements with atomic numbers greater than 20 and energies in the 10 to 30 keV range. In an effort to increase sensitivity, the use of synchroton x-radiation has been explored for the potential development of a reference method for the certification of trace element SRMs. The use of highly intense, polarized and monochromatic x-rays, tunable from 5 to 20 keV in total reflection geometry makes elemental analysis possible down to ppb levels.

Future research in the Division includes a diverse range of interests. Ion beam analysis by secondary ion microscopy will be extended to realize complete three-dimensional compositional mapping which, in conjunction with the Nuclear Analytical Methods Group, will hopefully develop into the first NBS ion implant depth profiling SRM. In the area of molecular microanalysis by LAMMA, a program will be implemented to examine pattern recognition techniques for spectrum analysis. In the area of electron analysis, investigations into low-energy microanalysis of solid specimens will be initiated. Application of total reflection XRF using synchroton radiation will be oriented toward the measurement of selenium in human serum.

Other research will include an investigation of sources of methane, carbon monoxide, and elemental and organic carbon in atmospheric particles on an urban to global scale, and also the investigation of trace carbonaceous particles will be extended to the paleoatmosphere through recovery of particles from polar and midlatitude ice cores. In the area of spectroscopy, investigations to ferret out systematic errors in diode laser measurements will continue along with the determination of absorption coefficients for reactive radicals such as HO_2. Gas standards research will include the development of a dynamic HNO_3 generation system for sub-ppm levels, implementation of procedures by which EPA can calibrate a mobile TDLAS unit for NO_2, finalization of the evaluation of isotope dilution mass spectrometry as an absolute reference method for determining CO_2 at ambient concentrations, development of multicomponent toxic organic cylinder standards for EPAs group four compounds at the ppb level, and the evaluation of trace analysis protocols and standards to provide data quality assurance in the analysis of gaseous mixtures for NASA's space shuttle program.

1. Microanalysis Group: Overview

The Microanalysis Research Group carries out research to advance the development and application of 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, inelastically scattered electrons, inelastically scattered photons, or ions. The techniques employed by Group members include electron probe microanalysis (EPMA), scanning electron microscopy (SEM), analytical electron microscopy (AEM), electron energy loss spectrometry (EELS), secondary ion mass spectrometry (SIMS), laser microprobe mass analysis (LAMMA), and laser Raman microanalysis (LRM).

Research is conducted on several aspects of each technique, including (1) advancing understanding of the basic physics of sample excitation by the primary radiation and of the propagation of the secondary radiation, (2) developing methods of quantitation, (3) producing standards and techniques as a means of disseminating developments, (4) applying results of the research to developing improved compositional mapping techniques, and (5) the study of specific analytical problems in aid of NBS and other government agency activities as well as national scientific priorities.

During FY86, the members of the Group 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:

(1) Electron Beam Microanalysis

Compositional mapping has continued to be a major theme for much of our work. In electron probe microanalysis, the successful development of a compositional mapping technique for use with wavelength-dispersive x-ray spectrometry, first described in FY85, has been significantly modified and improved. A new method has been developed which makes direct use of a spectrometer wavelength scan across a peak to provide the basis for mathematically constructing a "standard map" for subsequent calculation of the k-value map for the unknown. This procedure results in significant benefits by eliminating the time required for acquiring the standard maps and by improving the statistical quality of the data for the standard, since the much smaller number of channels needed for the peak scan allows longer counting time at each channel. The new procedure should make compositional mapping more readily applicable to practical problems.

In scanning electron microscopy, the acquisition of a new high resolution analytical scanning electron microscope has stimulated our research in both imaging and analysis problems. The visibility of asbestos fibers as a function of sample preparation technique and electron optical conditions has been studied to aid in the development of test samples for the Environmental Protection Agency.

In analytical electron microscopy, the advanced image processing system for the AEM has undergone additional development. Rapid exchange of images has been demonstrated between the VAX 11/730 computer which handles the instrument automation and the VAX 11/780 computer, in which the image processor and the higher level image processing algorithms reside. This computer network will provide access to the sophisticated image processing techniques developed in the LISP-based procedures on the VAX 11/780, including automatic control of the beam position on the specimen based on the results of image processing. The analytical capabilities of the AEM have been extended by the inclusion of an ultrathin window energy dispersive x-ray spectrometer, which allows measurement of x-ray energies as low as 185 eV (B K x-rays) and a high purity germanium energy dispersive x-ray spectrometer, which can measure x-rays with energies up to 150 keV. These spectrometers provide access to the entire range of characteristic x-rays, except for those of the very lightest elements.

(2) Mass Spectrometry Microanalysis

The automatic measurement of isotopic ratios of arrays of discrete particles viewed in the ion microscope, a form of secondary ion mass spectrometry, has been accomplished. The image processing software operates on digital images recorded by a TV camera which views the fluorescent screen of the ion microscope. The computer image processor automatically recognizes particles, corrects for background, and calculates isotopic ratios from a series of images taken at various masses. The limits to the accuracy and precision of measurements from a camera-based imaging system are being evaluated.

The data recording capability of the laser microprobe mass analyzer has been greatly extended by the incorporation of a pair of digital transient recorders with 32 kilobyte memory capacity, which allows recording at two sensitivities of the complete mass spectrum from hydrogen to the actinides on every laser shot. Using the new data handling capability, a research program has been installed to measure interelement effects on the quantitative analysis of multi-element glasses in the form of films and particles.

(3) Molecular Microanalysis

Studies of molecular microanalysis with the laser microprobe mass analyzer have been extended to a study of carbonate compounds, under the impetus of developing techniques for the chemical analysis of individual mineral particles. The molecular species produced under laser ablation from various compounds have been studied in detail to attempt to resolve certain difficulties in reproducing results reported in the literature by other workers. Results suggest that the formation of carbonate ion species in the LAMMA spectrum is dependent on the cation present and the laser irradiation conditions. Also, certain artifacts which arise from substrate contributions to the spectrum have been recognized.

In the area of laser Raman microanalysis, progress has been made on applications of the technique to molecular microanalysis for biological problems. LRM represents one of the most promising molecular microanalysis techniques for application to biotechnology, so that special efforts have been concentrated in this area.

Future Plans:

In the area of electron analysis, the digital imaging system will be extended to include digitization of the conventional transmitted electron images and diffraction patterns, which will greatly extend our analysis capabilities. Image processing algorithms will be developed for direct solution of electron diffraction patterns from the fundamental characteristics of the pattern with minimal operator intervention. The electron energy loss signal will also be utilized for compositional mapping images. Investigations into low-energy microanalysis of solid specimens will be initiated.

Further advances in the development of quantitative EPMA are limited by the existing data base of quantitative measurements on known standards and of the fundamental parameters which are incorporated in the physical models of electron beam specimen interactions. The limitations on the k-value data base from standards will be addressed during the next year by initiating a project involving a guest worker to make comprehensive measurements on the suite of special standards which have bee developed within the Group in recent years. During the past year, the Group has also investigated the feasibility of developing an electron/x-ray optical bench which will permit the measurement of fundamental parameters. Preliminary design work has been completed, and we plan to implement these designs in the next year to produce an initial instrument.

Ion beam analysis by secondary ion microscopy will be extended to demonstrate quantitative analysis both laterally and in-depth to realize complete three-dimensional compositional mapping. As part of this work, we plan to develop in conjunction with the Nuclear Analytical Methods Group the first NBS ion implant depth profiling SRM. The camera-based digital imaging system will be augmented to permit quantitative measurements over a much larger dynamic signal range. The quantitative measurement of concentrations by imaging methods is a high priority for development. An opportunity also exists for collaborative work with the sub-micrometer scanning ion microprobe of Prof. R. Levi-Setti at the University of Chicago. We will attempt to investigate the utility of this instrument for isotopic analysis of sub-micrometer particles.

In laser microprobe mass spectrometry, a major limitation to the quantitative use of the technique arises from the poor reproducibility of the ion source (laser beam - specimen interaction) and the non-linear response of the signal measurement process. A systematic effort is planned to study the entire signal generation and processing chain. In addition, experiments to investigate the possibility of separating the atom transport and the ionization stages by use of two laser pulses separated in time will be carried out. In the area of molecular microanalysis by LAMMA, a program has been implemented to examine pattern recognition techniques for spectrum analysis. This program includes the interfacing of the LAMMA data output to the VAX computer to provide for the higher level of computation and mass storage required.

Dale E. Newbury, Group Leader; Adville A. Bell, David S. Bright, Peter H. Chi, Edgar S. Etz, Robert A. Fletcher, Ryna B. Marinenko, Robert L. Myklebust, Thomas R. Pereles, Patrick J. Sheridan, David S. Simons, John A. Small, Eric B. Steel, and Barbara B. Thorne.

2. X-Ray Fluorescence Group: Overview

Improvement of the accuracy and sensitivity of x-ray fluorescence spectrometry continue to be long term research goals of this group. The accuracy of fundamental constants required in first principle calculations for correction of matrix effects for quantitative analysis is of primary interest. This year we examined three commonly used compilations of mass absorption coefficients to determine any influences in the results of analysis which could be ascribed to the different compilations. For improving analytical sensitivity via sample preconcentration, several approaches are being explored to develop specific chelator membranes. We have investigated the potential of using synchrotron x-radiation in so-called total reflection geometry for ultratrace analysis and especially for application to certification analysis of trace element SRMs. A major portion of our work continues to be the quantitative analysis and homogeneity testing of new and renewal SRMs and the fabrication and characterization of new thin glass films for XRF calibration.

A major accomplishment during the past year has been the publication of a paper describing the effects of different sources of mass absorption coefficients in fundamental parameter (first principle) computer programs on the results of analysis. One finds when comparing three commonly used compilations that differences of 10% or larger are often found for elements with atomic numbers greater than 20 and energies in the 10 to 30 keV range.

We are investigating a commercially available fluorocarbon polymer membrane in addition to cellulose filter papers for attachment of specific chelating ligands for sample preconcentration. An automated closed-system apparatus has been constructed for performing the activation with subsequent attachment of the chelating groups to the substrates.

In addition to the development of sample preconcentration techniques for enhancing analytical sensitivity, the use of synchrotron x-radiation was explored for the first time by this group for the potential development of a reference method for the certification of trace element SRMs. The use of highly intense, polarized, and monochromatic x-rays, tunable from 5 to 20 keV, in total reflection geometry makes elemental analysis possible down to ppb levels.

Several Marine and NOAA samples were analyzed by XRF as part of an NBS-NOAA Specimen Bank Project. In the National Status and Trends program, NOAA (National Oceanic and Atmospheric Administration) monitors the levels of both organic and inorganic pollutants in 50 coastal cities around the U.S. NBS banks samples from twelve of these sites and performs quantitative analysis of selected samples.

During the past year, several types of alloys were tested for homogeneity and quantitatively analyzed. These include SRMs 1685B, 1686B, 1687B, 2631, and 2632. Proposed SRM 679 (Brick Clay) and SRM 88b (Dolomite) were also analyzed, the results of which are used in the certification of these materials.

Future Plans

In the area of sample preconcentration, we expect to evaluate the performance of prototype chelator membranes for trace analysis using typical SRMs. Additional work on the application of total reflection XRF using synchrotron radiation will be oriented towards the measurement of selenium in human serum. The development of new thin films for XRF calibration will include candidate thin samples for sulfur calibration. Finally, the testing of homogeneity and analysis of materials for OSRM will continue.

Peter A. Pella, Group Leader; Anthony A. Marlow, John Sieber, Gerald Sleater, and Wang Ziyao.

3. Atmospheric Chemistry Group: Overview

Research activities of the Atmospheric Chemistry Group are directed toward a) the development of a program in Chemometrics which employs advanced mathematical statistical methods together with expert chemical knowledge for the design and evaluation of complex, multicomponent chemical measurement processes, and b) the development of standard reference instruments and advanced methods of measurement of atmospheric ozone and trace carbonaceous gases and particles. Cooperative research activities with scientific institutions in this country and abroad continue to focus on increasing our knowledge of trace chemical perturbations of the atmospheric system by anthropogenic and natural processes.

The ozone calibration facility provided service during the past year to industrial laboratories and to U.S. and Canadian government laboratories. The EPA ozone monitoring network was augmented with the delivery of two additional Standard Reference Ozone Photometers (SRP). Also, a stable ozone generator was developed for possible use as a secondary ozone standard. The sensitivity of the ozone absorption cross section instrumentation is being increased to permit measurements in the 400-600 nm range; a possible byproduct of this effort will be an improvement in ozone SRP sensitivity to 0.06 ppb.

Chemometrics activities have emphasized detection limits, quality assurance, multivariate microanalysis, and planning for an integrated chemometric approach to the chemical measurement process. Fundamental and applied aspects of the limit of detection in analytical chemistry was the subject of a two day symposium organized by the group leader for the spring 1986 National

American Chemical Society (ACS) meeting. The substance of the symposium will be published by the ACS in their symposium series early in 1987. Detection limit concerns of the International Atomic Energy Agency (IAEA) in their Intercomparison and Cooperative Research Programs were addressed via a Consultants' Meeting, called by the IAEA and chaired by the group leader. A document resulting from the meeting will provide a unified approach for the evaluation of detection limits for a variety of trace analysis methods utilized in IAEA programs. Special attention is being given in this document to the confounding effects of difficult chemical matrices and blanks.

This year's research has focused on the effective extraction of chemical information from multidimensional signals in multicomponent systems. Initial studies in this area are treating laser mass spectra of microscopic samples of organic polymeric particles and a continuous multielement glass film. Factor analytical techniques are being successfully applied to estimate the instrinsic dimensionality (number of independent factors) and to select the mass fragments carrying the greatest discriminating power. Applications of this work are anticipated in investigations of multicomponent microhomogeneity, interlaboratory trace analysis, and source apportionment of individual atmospheric particles.

Source apportionment of bulk atmospheric, carbonaceous particles and gases has continued with important collaborative efforts with the EPA, Sandia National Laboratory, the University of Arizona, and the Norwegian Institute for Air Research. The work at Arizona, together with some cooperation also with the University of Pennsylvania, has focussed on basic advances in the measurement of natural levels of ^{14}C in trace levels of atmospheric carbon. A microsample preparation system developed at NBS has made it possible to prepare excellent targets for accelerator mass spectrometry (AMS) with less that 100 μg carbon in the original atmospheric sample. Extremely efficient and clean sample preparation techniques have been responsible for this success. Among the ^{14}C measurements completed with this technique have been samples of atmospheric methane and carbon monoxide, plus carbonaceous aerosols from Norway, Alaska, New Mexico and North Carolina.

Most of the ^{14}C measurements concern the issue of urban pollution, especially the discrimination of CO and particles from woodburning and fossil fuel combustion. ^{14}C is probably the most reliable discriminating species for this type of problem. As a result, it is being used to estimate directly the source contributions, and also to calibrate or validate indirect methods based on patterns of trace elements or polycyclic aromatic hydrocarbons (PAH). Investigation of the origins of elemental and organic carbon, including the PAH, constitutes the major thrust of the cooperative research in the EPA's Integrated Air Cancer Program.

Future plans for the Atmospheric Chemistry Group include: a) extension of the Chemometrics effort toward the development of an integrated approach to the chemical measurement process (CMP) including exploratory and expert systems considerations for CMP design; this would be followed by iterative techniques of method optimization and data evaluation, and application to selected research problems in the Center; b) completion of the EPA ozone monitoring network, with the delivery of the final two SRP's early in 1987; c) extension of the sensitivity of the ozone SRP's, and exploring their applicability to other atmospheric trace gases; d) investigation of sources of methane, carbon monoxide, and elemental and organic carbon in atmospheric particles on an urban to global scale, in parallel with the development of complementary isotopic

(^{13}C, ^{14}C) and PAH pattern recognition. The investigation of trace carbonaceous particles will be extended to the paleoatmosphere through recovery of particles from polar and midlatitude ice cores, in a program which would involve cooperation among a number of organizations, including NBS, the National Science Foundation, and the University of Arizona.

Lloyd A. Currie, Group Leader, Arnold M. Bass, George A. Klouda, James E. Norris, Will Ollison, Ann E. Sheffield, T. Stafford, J. M. Sullivan, P. E. Hare and V. Mohan.

4. Gas Metrology Research Group: Overview

The Gas Metrology Research Group conducts research on preparative and analytical techniques for the development and quantitative assessment of trace gas mixtures, investigates the measurement uncertainty associated with the preparation and analysis of these mixtures, conducts evaluations to discern their short and long term stability, and develops basic data to characterize their fundamental spectral, chromatographic, and detection properties. Preparative techniques used to develop primary standards for calibrating the trace gas measurements include pressure-vacuum manifold systems, precise and accurate gravimetry, dynamic dilution systems, and gas blending. Analytical techniques include gas chromatography, mass spectrometry, non-dispersive infrared analysis, chemiluminescence analysis, Fourier-transform infrared and diode laser spectroscopy, and various analytical systems for the determination of trace gaseous impurities.

This research is applied to a) the improvement of measurements for ambient, trace, and ultra-trace gas analysis, and to b) the development of accurate and stable single and multi-component standards for a wide variety of inorganic gaseous and organic vapor mixtures ranging in concentration from the percent to the part-per-billion (ppb) level. These standards are developed and maintained as primary calibrants for national and state regulatory programs, industrial, institutional, and federal measurements, international collaborative programs, and global monitoring programs. The Group directly responds 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. Utilizing its unique capabilities, the Group also performs a limited number of gas analyses for external organizations.

During FY86, Group research activities have included: (1) an extensive evaluation of the errors associated with the gravimetric procedure used for the development of high accuracy gaseous SRMs for global monitoring of atmospheric carbon dioxide, (2) the development of multi-component standards of volatile toxic organics in the low ppb range to provide data quality assurance for EPA's national ambient and hazardous waste incineration audit programs, (3) the completion of a portable tritium calibration system for the calibration of measurements of ultra-trace levels of atmospheric tritium, (4) the completion of a stable standard for sulfur dioxide in air at 100 ppb and a 100:1 dilution system for calibration of sulfur dioxide in ambient dry acid deposition measurements over the concentration range of 1-100 ppb, (5) the analytical measurement of the strengths of infrared absorption bands of halocarbons F-11 and F-12 at stratospherically-relevant temperatures, (6) an assessment of errors associated with the use of single- vs. multi-component hydrocarbon standards in the analysis of natural gas mixtures, (7) an initiation of the development of multi-component gas standards for automotive emission testing for EPA and State IM programs, (8) feasibility studies for the development of stable standards of hydrogen sulfide for calibrating reduced sulfur emissions by the pulp and paper industry, and (9) the certification analyses to restock about 20 gaseous SRMs.

Two major accomplishments during the past year have been: (1) a rigorous evaluation of the methodology used for preparing highly accurate primary gravimetric standards for carbon dioxide in air used for the certification of stable SRMs in the 300-400 ppm range, having a concentration uncertainty of less than 0.1 percent relative at 95 percent confidence; and (2) the development of a 17-component mixture of volatile toxic organics to calibrate GC/MS analyses of ambient air samples. Research in the former area has led to the development of an optimized procedure that minimizes errors due to the transfer of pure carbon dioxide into primary standards during their preparation and to the effects of differences in the matrix air employed. Research in the latter area has resulted in an NBS-traceable standard that has been used by EPA/EMSL/RTP for calibrating GC/MS measurements of air samples obtained from an accidental chemical emission in the vicinity of a major urban area.

Future Plans:

Further developmental activities planned for atmospheric level Carbon Dioxide-in-Air SRMs include: the finalization of the evaluation of isotopic dilution mass spectrometry as an absolute reference method; certification of SRMs at 300 and 360 ppm; the establishment of a set of about six such SRMs that will continue to bracket global atmospheric carbon dioxide levels for the indefinite future; and collaborative studies in working with other Federal agencies and with the World Meteorological Organization in laboratory intercomparisons to ensure an international consistency in ambient carbon dioxide measurements. Research in the area of volatile toxic organic standards will include the development of ppm and ppb multi-component mixtures for EPA's Group Four compounds and the development of preparative methodology for seven-component mixtures at 5 ppb for State monitoring programs. Other planned research activities include the development of electrochemically-based gas analysis methodology, the development of ppb mixtures of nitric oxide for dry acid deposition studies, and the evaluation of trace analysis protocols and standards to provide data quality assurance in the analysis of gaseous mixtures for NASA's space shuttle program. The Group also will continue to provide certification analyses to maintain the availability of gaseous SRMs, currently totaling about ninety different.

Group staff changes during the year have included the interagency transfer of Dr. James Elkins in late FY86 to NOAA/GMCC in Boulder, CO, and his replacement with Dr. Michael Verkouteren. Dr. Verkouteren has completed a post-doctoral appointment with Dr. Lloyd Currie in our Division, and comes to us with experience in gas analysis, mass spectrometry, and low-level radioactivity measurements. The Guest Worker appointment of Mr. Zhong-tao Cai (Shanghai Institute of Ceramics, People's Republic of China) was extended through December 1986. Correspondence is in progress concerning the possible appointment of a second Guest Worker from the People's Republic of China in trace gas analysis.

More detailed write-ups of selected activities and accomplishments of the Gas Metrology Research Group during FY86 are provided in the Technical Activities section.

Walter L. Zielinski, Jr., Group Leader; Zhong-tao Cai, William F. Cuthrell, William D. Dorko, Ernest E. Hughes, Rudolph von Kelly, Gerald D. Mitchell, W. Robert Miller, Richard C. Myers, George C. Rhoderick, James E. Suddeuth, Michael Verkouteren.

5. Analytical Laser Spectrometry Group: Overview

The Analytical Laser Spectrometry Group conducts research on the development, characterization and application of state-of-the-art laser-based spectroscopic techniques for the detection of trace and ultra-trace level gaseous atmospheric constituents. The analytical techniques utilized include a) photoacoustic spectroscopy, b) phase fluctuation optical heterodyne detection, c) photothermal deflection, and d) tunable diode laser and Fourier Transform IR (FTIR) absorption spectrometry. A primary objective of the research carried out in the group is the improvement of measurement sensitivity, selectivity and accuracy of these various techniques for the analysis of trace reactive atmospheric gases. Other objectives include: (1) development of new calibration approaches for the above laser-based techniques, (2) measurement of fundamental molecular parameters necessary for quantitative spectrometry such as infrared absorption, pressure-broadening and collisional-narrowing coefficients, (3) intercomparison of concentration determinations by various techniques, and (4) application of tunable diode laser spectrometry in the verification of gas standard concentrations and in kinetic measurements of transient species.

As in the past year, the group's activities throughout FY86 have focused on fundamental and applied research utilizing tunable diode laser absorption spectrometry (TDLAS). Four different, but closely related, research topics were pursued. As will be further detailed in the selected technical reports that follow, these research activities include the (1) determination of absorption and pressure-broadening coefficients for selected nitrogen dioxide (NO_2) lines in the infrared, (2) the reinvestigation of the gas phase titration (GPT) reaction between nitric oxide (NO) and ozone (O_3), (3) the construction and characterization of a highly accurate dynamic NO_2 calibration system, and (4) the development of a nitric acid (HNO_3) calibration system for dynamic standards in the parts-per-million (ppm) concentration range.

Accurate molecular parameters, such as absorption and pressure-broadening coefficients, for important atmospheric gases like NO_2 are essential for both laboratory and atmospheric studies. Traditionally, such determinations for NO_2 have been carried out using only pressure measurements to derive the number density of the absorbing species. Because of the presence of N_2O_4 and the reactive nature of this compound, systematically low absorption coefficient results are likely to occur employing pure samples of NO_2, unless special precautions are taken. To address this problem, a novel approach was developed in our laboratory this past year which completely eliminated the possibility of such error sources. This was achieved utilizing dynamically generated NO_2 standards in the 50-100 ppm range employing specially prepared permeation tubes. In this way, the absorption cell was continuously exposed to new sample gas. More importantly, this approach enabled us to determine the concentration of the sample gas with a great deal of redundancy employing gravimetric, Fourier transform infrared and gas phase titration techniques. Using this approach, absorption and pressure-broadening coefficients for over 26 different vibration-rotation lines of NO_2 in one of the most important spectral regions of the infrared (the ν_3 band at 6.2 μm) were determined.

Significant progress has also been made this past year on the group's long term goal of improving the photometric accuracy of TDLAS measurements. Employing the techniques, line-fitting algorithms and system improvements discussed in last year's report, we have been able to identify and characterize a subtle, but major, systematic error source not heretofore reported. In measuring gas concentrations by TDLAS, or alternatively in determining absorption coefficients, the peak absorbance at the center of the absorption feature under study is typically measured. It has been well established that such determinations can be systematically low by as much as 50% when the laser exhibits an appreciable linewidth relative to the absorption feature under study. The shape of the resulting absorption profile becomes clearly distorted, as manifested by an increased absorption linewidth. However, the integrated absorbance across the absorption feature will be unaffected by this "excess laser linewidth." With this in mind, many investigators typically correct determinations based upon peak absorbance measurements using the increased absorption linewidth as a scaling factor. This is accurate as long as no other causes of increased linewidth are prevalent. However, our investigations reveal that laser frequency-jitter, due to mechanical shocks from the closed-cycle refrigerator compressor, also causes an increased absorption linewidth. In contrast to excess laser linewidth, this compressor frequency-jitter does not affect the peak absorbance but rather the integrated absorbance. In this case, determinations based upon the peak absorbance would be accurate while those based upon the integrated absorbance, or corrected for the increased width, would be systematically too large by as much as 12%. As a result of these two opposite effects, and their associated systematic errors, all determinations carried out in our laboratory utilize both peak and integrated-fit absorbances. In addition, a unique microphone-triggering circuit has recently been completed which tracks the motion of the compressor piston and allows data to be taken only during the central portion of the cycle. This eliminates the mechanical shock responsible for the compressor frequency-jitter.

Significant progress has also been achieved this past year in reinvestigating the stoichiometry of the gas phase titration reaction between NO and O_3 to produce NO_2. As in our past studies carried out four years ago, all three constituents were measured employing independent techniques. Significant improvements, however, in both the generation and measurement of O_3 as well as the measurement of NO_2 were incorporated in the present study. Throughout these measurements, the measured O_3 concentration was found to be consistently lower than the concentrations of the other two constituents by 1-1.5%. Various precautions were taken to ensure that other photochemical oxidants, such as HO_2 and CH_3O_2, were not simultaneously involved in titrating NO to NO_2. Work is continuing on this project. However, our results to date suggest that the presently accepted value for the O_3 absorption cross section at 254 nm may have to be lowered by 1-1.5%, in almost exact agreement with results recently obtained by Mauersberger employing a completely different technique.

Research planned for the upcoming year will continue many of the efforts initiated this past year. In particular, research will focus on employing TDLAS in: (1) continuing the reinvestigation of GPT, (2) studies to characterize HNO_3 in high concentration NO_2/air compressed air cylinders, (3) research efforts to continue the development of a dynamic HNO_3 generation and calibration system for ppm and sub-ppm concentration levels, (4) the implementation of procedures and protocols by which EPA can calibrate a mobile TDLAS for field measurements of NO_2, (5) the continued investigation of systematic error sources, and (6) in the determination of absorption coefficients for reactive radicals such as HO_2.

Alan Fried, Group Leader; Robert Sams, Barry Cadoff, Patricia Johnson, Linda Nunnermacker, and Nathan Yates.

B. Selected Technical Papers
(Gas and Particulate Science Division)

1. Continuum Radiation Produced in Pure-Element Targets by 10-40 keV Electrons: An Empirical Model

J.A. Small, S.D. Leigh, D.E. Newbury, and R.L. Myklebust

The purpose of this work was to generate a comprehensive x-ray continuum database and develop an empirical expression for continuum emission by modeling the data. The data set used in this study consisted of approximately 4100 continuum x-ray intensity values. The intensity of the continuum I_ν, is a function of the atomic number of the target, Z, the energy of the continuum x-rays, E_ν, and the energy of the incident electrons, E_0. The targets used in the study were opaque to the electron beam and consisted of 44 pure elements ranging in atomic number from Z=4 to Z=92. E_0 values of 10,15,20,25,30,35, and 40 keV were investigated for this study.

The modeling of continuum x-ray production was done on generated x-ray intensities, i.e., the intensity per unit of electron flux produced within the target. The experimental intensities were selected so that they were free of characteristic and escape peaks as well as other major spectral artifacts. The calculation of the generated continuum x-ray intensities from experimental x-ray intensities required correcting the data for absorption of x-rays by the target material and the detector, electron backscatter loss, and anisotropic x-ray generation. No corrections were made for the escape of Si x-rays from the detector, incomplete charge collection, and the absorption of x-rays in the 20 nm thick carbon coat on the sample. For continuum measurements, these corrections are relatively insignificant and will have a minimal effect on the final model. In addition, the final equation does not include a geometric efficiency term.

Our basic approach in developing a parametric empirical model to describe the data was to employ graphical methods to analyze the data by plotting various portions of it in 2-, 3-, and 4-dimensional representations. For this work, I_ν, was consistently used as the dependent variable. These plots were then fitted in an iterative fashion with models suggested by the observed shapes. The modeling was done with the NBS DATAPLOT program. The 2-dimensional plots were modeled first. The information from the fits run on the 2-dimensional plots was then combined to model the 3- and 4-dimensional surfaces. The final model can be expressed in photons-per coulomb-per 10 eV energy window as:

$$\log(I_\nu) = \{M\log(Z[E_0/E_\nu - 1]) + B\} \qquad (1)$$

where $M = 0.0060E_0 + 1.047$; $B = -0.032E_0 + 5.799$

This relation incorporates the well-known Kramers' variable, $Z*(E_0/E_\nu - 1)$, into a global model useful for predicting generated continuum intensities over a wide range of accelerating voltages 10-40 keV, atomic numbers 4-92, and x-ray energies 1.5-20 keV. It was determined from the mathematical modeling of an extensive data set that includes a broad range of E_0's and E_ν's and a majority of the pure-element targets which are usable in electron beam instruments. In general, under normal analysis conditions, relative errors less than 20 percent can be expected for intensities calculated with this equation.

2. Defocus Modeling for Compositional Mapping with Wavelength-Dispersive X-ray Spectrometry

R.L. Myklebust, D.E. Newbury, R.B. Marinenko, and D.S. Bright

Quantitative compositional mapping by electron probe microanalysis with wavelength-dispersive x-ray spectrometry provides a new and important mode of operation. The use of the wavelength-dispersive x-ray spectrometer (WDS) provides access to trace compositional levels but, in order to employ the WDS, a correction must be applied to the data to compensate for the effects of spectrometer defocusing. There exist four methods to correct spectrometer defocusing: (1) stage scanning; (2) spectrometer crystal rocking to move the focus position of the spectrometer in synchronism with the beam scan on the specimen; (3) "defocus mapping," described in our work for FY85, in which a "standard map" is prepared under the same conditions as the unknown and is used to calculate intensity ratios with the map of the unknown on the basis of corresponding pixels; and (4) "defocus modeling," in which the defocus map is calculated rather than directly measured.

While the standard map technique can provide accurate corrections for defocusing, there are significant drawbacks in the practical application. (1) Preparing the standard map requires scanning an area on the standard as large as that of the unknown. (2) Any defect in the standard such as a scratch, hole, or inclusion which affects the x-ray intensity will appear as an artifact in the final compositional map of the unknown. (3) Although the standard maps can be archived and readily scaled to changes in beam current or spectrometer efficiency, a new map is required for each new magnification and element. Defocus modeling can overcome several of these limitations and provide a more flexible approach to mapping.

The principle of defocus modeling is based on the observation that an x-ray area scan which is generated with a moving electron beam and a fixed spectrometer contains equivalent information to an intensity profile of an x-ray peak generated by scanning the spectrometer with a fixed beam. Thus, if we have a spectrometer scan across a peak measured on a standard, which consists of the intensity as a function of angular position, it should be possible to construct an equivalent "standard map." The procedure used to calculate a standard map is to first determine two points on the line of optimum focus in the scan matrix, which can be recognized in the intensity map of the unknown. For each location (i,j) in the standard matrix, the distance from the focus line is then calculated. This matrix distance is converted into a angular deviation which corresponds to a particular excursion off the peak in the spectrometer scan of a standard. From this equivalent position in the peak scan vector, the intensity, I, relative to the peak centroid is taken and assigned to matrix location (i,j,I). The procedure is repeated until the standard map matrix is completed.

In order to test this procedure, a defocus map was generated by the modeling method and compared to a defocus map generated by the scanning method. The disagreement between the trace from the synthetic standard map and the trace from the experimental standard map is less than 2% throughout the range. There are several advantages of defocus modeling. Only one peak scan of sufficient angular width is needed to generate a standard map appropriate to any magnification in the range covered. The calculation procedure from stored scan vectors is inherently fast. The modeling procedure is useful down to magnification of approximately 150x, being eventually limited by statistical considerations due to the fall-off in spectrometer transmission. The synthesized standard map can have better counting statistics than a conventionally scanned standard map because longer counting times per channel can be allowed when making the peak scan.

3. Bright Field Image Correction Using Various Image Processing Tools

D.S. Bright and E.B. Steel

Many microscopes, whether using light or electrons, have trouble maintaining uniform illumination across a field of view at the lowest magnification ranges available on the instrument. This is because the microscope optics and detectors are primarily designed for higher magnification viewing. However, uniform background illumination is desirable not only for display but for subsequent computer analysis.

Elementary calculations show that a bright field or transmission mode image may be corrected for uneven background illumination and non-uniform detector sensitivity by dividing the image by a background or blank image. Images typically corrected by this method are taken at low magnification, e.g., 40X on a compound light microscope (LM) or 300X on a Scanning Transmission Electron Microscope (STEM). The correction is made by dividing the image by a blank or background image, with appropriate filtering, and then by scaling the result. When blank images are not easily obtained instrumentally, and when the objects in the image are sufficiently thin or small, the background image may be approximated using the sample image by applying a maximum filter. The maximum filter is a smoothing filter where each pixel of the generated blank image is the maximum value of the original pixels in a square window around it. The window should be about twice as wide as the largest narrow dimension of any feature in the sample image.

The rationale for dividing an image by a blank image is the following:

For each pixel:

$$I = L * A * S \qquad \text{(a)}$$

where I is the pixel intensity, L is the illumination for that pixel, A is the fraction of radiation transmitted by the object, and S is the sensitivity factor of the detector. With no sample present, the pixel intensity, Ib, for the blank image is:

$$Ib = L * S \qquad \text{(b)}$$

Dividing equation (a) by equation (b) gives:

$$A = I / Ib. \qquad \text{(c)}$$

A is the desired intensity, to within a scaling factor, for the corrected image--one with even background illumination, and uniform detector sensitivity. Digital images corrected with this algorithm show the desired background uniformity and provide a better starting point for more sophisticated processing algorithms which seek to extract objects based on size and shape information or other criteria. This relatively simple background algorithm is thus a key to realizing better performance in the more complex image processing operations which are critical to our work.

4. Euclidian Distance Mapping for Shape Characterization of Alloy Grain Boundaries

D.S. Bright and D.E. Newbury

When monitoring the changes in microstructure of an alloy, as imaged with optical, electron, or ion microscopy, it may be desirable to characterize the shape of the grains of the discontinuous phase. In the course of examining some two-phase microstructures, the more common spatial parameters used to describe the structure, such as the phase intercept length, were not adequate to follow the complex changes observed in the structure. In particular, the discontinuous phase showed the formation of string-like protuberances.

A measurement that is sensitive to protuberances can be developed from the Euclidian distance map. The distance map is constructed from the original image by:

1. Setting a threshold intensity level to distinguish the discontinuous grains from the continuous phase.

2. Calculating the distance map for each grain.

3. Averaging selected values from the distance map over selected grains.

The choice of the threshold value is critical in such operations since the area, connectivity, and many other characteristics of each grain are affected. Often this choice is made by human operators, and therefore might not be reproducible. We have developed a computer algorithm that sets the threshold automatically, given that the edges of the grains in the image are sharp. The algorithm first takes the gradient of the image, which makes the edges of the grains the brightest objects in the image. Then a threshold level of this gradient image is chosen such that the edge areas selected have a maximum thickness of two pixels from the original image. The average intensity of the edge pixels is used as the threshold value. The distance map is then calculated using an efficient algorithm from the image processing literature. For pixels in each grain, values of the distance map represent the distance from the pixel to the nearest edge of the grain. The distance map has local maxima that lie on the skeleton of the grain. The value or height of the distance map at these points gives the width of the grain there. The average of the local maxima is a shape measure sensitive to the long thin protuberances which are attached to larger, more rounded parts of the grains. Rounded grains typically have a few large values, while the long, thin protuberances have many small values. The new measurement technique has been successfully applied to monitor changes in lead-tin alloys during annealing.

5. Ion Implantation Artifacts Observed in Depth Profiling Boron in Silicon by Secondary Ion Mass Spectrometry

D.S. Simons and P. Chi

We recently conducted and reported a comparison study of depth profiling by secondary ion mass spectrometry (SIMS) and neutron depth profiling (NDP) in collaboration with Division 551 and the NBS Center for Electronics and Electrical Engineering. The specimens were portions of 5 cm diameter single crystal <111> silicon slices in which ^{10}B had been implanted at various fluences and energies on the CEEE ion implanter. NDP measurements were made on a 13 mm diameter area at the center of the wafers. SIMS measurements were taken from a 60 μm diameter area approximately 16 mm from the center of the wafers.

One observation that emerged from this work was an apparent discrepancy between the profiles of ^{10}B measured by NDP and SIMS. The peaks of the SIMS profiles were typically deeper than those of NDP by as much as 30 nm, which is 10% of the projected range for a 70 keV implant. Moreover, the profiles could not be made to coincide by either a constant shift or a proportional change of one depth scale with respect to the other. The discrepancy was not explainable by any known artifact of either SIMS or NDP. This led to a hypothesis that the actual depth distribution of boron in the wafers was not laterally homogeneous. We have conducted two experiments to check this proposed explanation. In the first case, SIMS profiles of ^{11}B were taken at 5 mm intervals across two perpendicular diameters of a 5 cm diameter wafer of <111> silicon that had also been implanted at the CEEE facility. Discrepancies in the depth of the peak as large as 25 nm were seen between the edge and center of the wafer, with the profile near the edge being deeper. Profile shapes were also different. These differences were not a smooth function of position along the diameter. Instead, all of the changes occurred from one edge to the center, and no differences outside of measurement variability were seen from the center to the other edge. The second experiment was a remeasurement by SIMS of several of the original wafers that had been implanted with ^{10}B, this time at the center of the same area that had been sampled by NDP. In this case the agreement of the two methods was within the limits of measurement variability.

The lateral inhomogeneity of boron that these experiments have demonstrated arises from the variable contribution of ion channeling during implantation. The single-crystal wafer is tilted 7 degrees from the surface normal in an attempt to achieve a "random equivalent" orientation that minimizes unintentional ion channeling. However, the ion beam is scanned by a single plate electrostatic deflection system that varies the angle of incidence by several degrees from one side of the wafer to the other. Since the fraction of incident ions that is channeled is a strong function of the incidence angle for angles less than 7 degrees, it is easy to understand how variations in ion channeling could occur across the wafer surface, resulting in differences in peak shape and projected range. Other factors that may contribute to this problem are the uncontrolled azimuthal angle of the wafer in the implanter and a possible misalignment between the center of the beam raster pattern and the center of the wafer. As a result of this new understanding of systematic effects in ion implantation, it is now possible to embark on a joint SIMS-NDP project to produce an ion-implanted depth profiling standard reference material for SIMS.

6. An Evaluation of A High Purity Germanium X-ray Detector on a 200 kV Analytical Electron Microscope

Eric B. Steel

The Microanalysis Research Group has tested the first high purity germanium detector (HPGE) to be used on an analytical electron microscope (AEM). Theoretical predictions and preliminary experimental results have been compared for the HPGE and Lithium-Drifted Silicon [Si(Li)] x-ray detectors which are simultaneously mounted on the microanalysis AEM.

A JEOL 200 CX AEM equipped both with a zero-degree take-off angle germanium detector and with a high take-off angle conventional Be window Si(Li) detector was used to collect data. NBS research material synthetic glasses, natural minerals, and pure metals were examined at an accelerating potential of 200 kV. The specimens were prepared as particles or sputtered films on thin carbon films supported by 200 mesh copper grids.

An AEM operating at an accelerating voltage of 200 kV is capable of exciting the K-line x-rays of all known elements, but the sensitivity of the Si(Li) x-ray detector mounted on these instruments decreases rapidly with increasing x-ray energy for the K-line x-rays of elements heavier than molybdenum (K-alpha = 17.44 KeV.) An attractive alternative for the high energy portion of the x-ray spectrum above 20 keV is the HPGE detector, which has been used for many years to analyze gamma-rays. The 5.6 mm thick HPGE has an efficiency greater than 90% for the K-line x-rays from the elements with atomic numbers from approximately 25 through 85. The Si(Li) detectors must rely on the observation of M and L-line x-rays for most elements above approximately atomic number 50.

Analysis with these high energy K-lines has certain advantages over the analysis of L and M-lines from the same elements: (1) The fluorescent yield is many times larger for the K-lines than the L or M-lines. (2) The continuum has lower intensity at high energies which improves the signal to noise for the high energy K-lines. (3) The absorption correction is very low for these high energy x-rays in the thin specimens analyzed on the AEM and in most cases can be ignored. (4) The K-line spectra are relatively simple with reasonably well known weights of lines. The M and L-line x-rays yield much more complex spectra with many more, often overlapping, peaks than are seen for K-lines. In addition, much less data is available on the relative weights of L and M x-rays than exists for the K-lines. Because of these problems with L and M-line x-rays, quantitation of heavy element compositions can be difficult.

The positive factors associated with the AEM x-ray analysis using an HPGC are tempered by several problems. The chief difficulty is the behavior of the ionization cross section. The cross section falls by a factor of ten from atomic number 50 to 96 when operating at 200 kV, so that although the high energy K x-rays are more efficiently detected they are less efficiently excited. Another disadvantage of the HPGE is the poor efficiency for the low energy x-rays from the elements with atomic number less than 20. This is largely controlled by the absorption in the Ge dead layer of the detector. Another factor which exacerbates the low energy problem is the large incomplete charge tails on the peaks in this region. These problems can be overcome by using the Si(Li) detector for analysis of the low energy x-ray lines.

7. Compositional Analysis of Human Cardiovascular Deposits by Micro-Raman Spectroscopy

E.S. Etz

In previous applications of Raman microprobe spectroscopy to the study of biological tissues, we have examined the processes of mineralization in tooth and bone with a view to obtaining data on the molecular composition from microscopic sampling regions. These studies have now been extended to other types of calcified tissues to further the present understanding of various forms of pathological calcification. The specific aim is to obtain a comprehensive physicochemical characterization of cardiovascular calcification in man employing a broad range of analytical techniques mainly to establish -- in the first phase of this work -- the complex identity of the inorganic or mineral phase of cardiovascular calcified deposits. The work described here is conducted in collaboration with researchers at the American Dental Association Health Foundation at the NBS under a grant from the National Heart, Lung and Blood Institute of the NIH.

Laser-Raman microanalysis (LRM) stands out as the only technique to provide direct molecular and structural information not available from the conventional electron- and ion-beam microanalytical techniques. Thus, LRM has corroboratively been applied to elucidate two types of cardiovascular calcification: (i) atherosclerotic calcification in man, and (ii) bioprosthetic calcification of heart-assist devices implanted in animals and in man. There is at present a special urgency about gaining a fuller understanding of the pathogenesis of biomineralization as it holds the promise of a more successful application in man of bioprosthetic cardiovascular devices. These investigations have relevance to certain areas of biotechnology, especially to current efforts of improving the blood compatibility of a wide range of biomedical polymers undergoing extensive evaluation as biological implant materials.

Of prime interest is the composition of the apatitic phase in native calcified deposits, and of deposits with the organic matrix removed by a deproteination treatment. Other goals are to obtain information on the type of carbonate substitution of CO_3^{2-} for either PO_4^{3-} or OH^- (or both) in these biological calcium phosphates, and to quantify carbonate contents by an empirical procedure employing calibration data derived from the measurement of synthetic carbonate apatites of known composition. The most abundant mineral in human tissues is a "biological" hydroxyapatite (HAP), idealized as $Ca_{10}(PO_4)_6(OH)_2$. But other calcium phosphates, for example $CaHPO_4 \cdot 2H_2O$ (brushite), $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ (octacalcium phosphate, OCP), and β-$Ca_3(PO_4)_2$ (β-tricalcium phosphate, β-TCP), have been identified with or without association with apatite. With age, and in most cases of pathological calcification, the phosphate minerals incorporate carbonate, forming stable phases of biological "carbonate apatites". In these, carbonate may substitute for phosphate (Type-B carbonate apatites) or for hydroxyl (Type-A carbonate apatites). Several types of cardiovascular calcified deposits were examined in the Raman microprobe furnishing diagnostic vibrational spectra. These consisted of human atherosclerotic deposits and of bioprosthetic calcified plaques removed from the "Blomer" (a widely used polyether urethane) surfaces of blood pumps implanted in both animals (calves and sheep) and in man. The Raman spectra of these deposits show a close similarity in composition of the mineral phase found in the different living organisms and associated with different host materials. It consists of an "impure" carbonate substituted (Type-B) hydroxyapatite for which carbonate contents are found to range from 5.8 to 7.5 wt%. These carbonate apatites of variable composition may be represented by the general empirical formula $(Ca_{10-x-y}(PO_4)_{6-x}(HPO_4, CO_3)_x(OH)_{2-x-2y}$, with substantial substitution of Ca by both Na and Mg. These results shed new light on the pathological processes leading to atherosclerotic disease and the degradation of bioprosthetic implant materials in the cardiovascular system. Furthermore, they point to similar mechanisms by which these deposits are formed.

8. Analysis of Molecular Carbonate by Laser Microprobe Mass Analyzer

R.A. Fletcher

There is considerable interest in detecting the presence of carbonates on the micrometer scale in biological bone apatites and in a recently discovered and extremely rare mineral. Owing to the low mass, carbonates are difficult to detect by electron microscopy, but can readily be detected by mass spectrometry. The analysis of carbonate in apatites by the Laser Microprobe Mass Analyzer (LAMMA) has been previously reported by one researcher. The LAMMA is a time-of-flight mass spectrometer that utilizes a pulsed laser to ablate and ionize the specimen in the micrometer domain. Attempts to reproduce the work quoted in the literature with the NBS LAMMA resulted in some anomalous observations, and a much more detailed study was undertaken as a result.

Mass spectra have been obtained for several alkali metal and alkali earth carbonates. Both commercial and high purity SRM material were examined. Dry crystals of each compound were suspended from a nickel transmission grid with no thin film backing. The samples were all irradiated with 266 nm radiation for a 10 ns pulse duration with power densities ranging from approximately 10^7 to 10^8 w/cm^2. The reported fragment ion useful for identifying carbonate is CO_3- m/z = 60. For the calcium, barium, and strontium carbonates, we have observed low ion formation at m/z of 60. The small m/z 60 peak is usually found in the presence of carbon clusters, C_{n-}, which appear at m/z 12, 24, 36, 48, 60, 72. However sodium, potassium, and to some extent lithium generate strong m/z 60 peaks. This is puzzling since the heats of formation for all the above compounds are approximately the same, -110 kJ/mole. What is of interest is that more soluble compounds tend to generate strong mass 60 peaks. The m/z 60 peak has been verified as the carbonate ion by using carbon 13 labeled isotopes of potassium and barium carbonate. The carbon cluster formation which is an interference at m/z 60 is from a carbon 12 contaminant, not from the fragmentation of the 99% $^{13}CO_3$. An understanding of the CO_3- abundance differences between alkali and alkaline earth carbonates is being sought.

The m/z 60 peak has been confirmed as the carbonate ion. However, the fact that the carbonate ion formation is so mysteriously weak for alkaline earth carbonates leads us to believe that the LAMMA in its current configuration will not prove to be a useful tool for analysis of biological samples where calcium carbonate is the species of interest. The further understanding of the interaction of alkali and alkaline earth carbonates with ultraviolet radiation may lead to some new knowledge of bond breaking and ionization processes in LAMMA. We are also interested in further developing the LAMMA with double-pulse ionization capabilities which may improve its sensitivity and specificity.

9. Ultratrace XRF Analysis with Monochromatic Synchrotron Radiation - Some Preliminary Observations

P.A. Pella and R.C. Dobbyns

Energy-dispersive x-ray fluorescence spectrometry is a technique often used as a routine analytical method because it is non-destructive, rapid, and capable of multi-element analysis. A major drawback is its relatively low sensitivity when compared to many other trace element techniques. Key factors to improving the minimum detection limit (MDL) consist of signal enhancement through higher x-ray intensity sources which are also energy tunable, and reduction of background. Recently, high sensitivity in XRF analysis has been demonstrated by using synchrotron radiation (SR) in which high brightness, energy tunability, and polarization of SR are effectively utilized. In the SR experiment, scattered radiation can be reduced owing to the effective utilization of the polarization of SR and to the use of a thin sample. In order to reduce the background still further, the use of total reflection of x-rays has been shown to be an effective technique. The combination of SR and total reflection geometry for XRF analysis has recently been applied by Iida and coworkers at the University of Tokyo at concentrations as low as 0.5 ppb or 1 pg.

The NBS Materials Science beam line has been operating at the Brookhaven National Laboratory for the past several years. This year we carried out preliminary experiments to determine if the existing experimental arrangement at the beam line is suitable for performing total reflection XRF analysis. We were also particularly interested to see if selenium in human serum could be analyzed non-destructively. There has been increased interest in the accurate determination of selenium at nanogram levels, especially for the development of human and bovine sera standard reference materials.

It was found that the present instrumentation at the beam line is ideally suited for performing total reflection XRF analysis in the 5 to 20 keV range using the monochromatic x-ray beam. This was determined using various types of samples on Si(111) reflector surfaces when the x-ray beam incident on the sample could be controlled and varied at angles below and above the critical angle, typically in the region of a few milliradians. A twenty microliter droplet of a human serum sample was allowed to evaporate on a Si(111) reflector and gave a Se signal which was about 2.3 times that of the background. These results indicate that Se at the nanogram level should be measurable by this technique. Further work will be directed towards the quantification of the Se x-ray intensity to determine concentration and to investigate the potential of the high flux white beam for ultratrace analysis.

10. Uncertainties in Mass Absorption Coefficients in Fundamental Parameter X-ray Fluorescence Analysis

P.A. Pella and B.A.R. Vrebos

Fundamental parameter correction methods for x-ray fluorescence analysis in the form of computer programs are becoming more common place in recent years. Programs such as NRLXRF, XRF-11, SAP3, and NBSGSC require physical constants such as mass absorption coefficients, fluorescence yields, and absorption jump ratios. When comparing programs, one finds that different sources of mass absorption coefficients are often used. Since there is no definitive compilation of mass absorption coefficients that x-ray analysts accept as being the most accurate, it was of interest to examine three commonly used compilations and to determine what influence, if any, could be observed on the results of analysis. These are the compilations of (1) Heinrich; (2) Leroux and Thinh; and (3) McMaster et. al. In addition, some fundamental computer programs use the total mass absorption coefficient (i.e., photoelectric plus coherent and incoherent scatter) while others just use the photoelectric contribution. The accuracy of any mass absorption coefficient can significantly affect the accuracy of results obtained when only pure standard samples are used for calibration and in so-called "standardless analysis." To test the influence of the different compilations on the analysis results, the program NBSGSC was used. This program offers several options, among which are choice of mass absorption coefficient compilations, measured or calculated primary spectral distributions, and selection of pure or multi-element standards for calibration. The influence of different sources of primary spectral distributions has already been published.

To obtain a perception of the relative differences in the mass absorption coefficient compilations over a broad range of atomic numbers and x-ray line energies, computer imaging was used to compare the individual values between any two compilations and to display the relative differences. From these figures it was surprising to see differences greater than 10% for elements with atomic numbers larger than 20 and energies in the 10 to 30 keV range.

To detect any direct influence of mass absorption coefficient differences in results of analysis, an analysis strategy had to be devised. Sample matrix and incident x-radiation energy had to be chosen when the mass absorption coefficient differences in compilations were significant. For this reason, we chose to perform an energy-dispersive experiment using different secondary target exciters in order to select monochromatic primary radiation of known energy. In this way, uncertainties in the incident x-ray spectrum are minimized. The samples chosen were Fe-Ni, and Fe-Ni-Cr alloys which exhibit strong interelement effects as well as strong absorption for the primary radiation. The secondary targets were zinc, germanium, molybdenum, and tin, covering a range from 8.6 to 25 keV for the incident energy. Both K_α and K_β lines of the secondary targets were considered for excitation where their ratio was measured from the scattered incident radiation from a light element sample. The samples were analyzed first with pure elements and then with "type" standard materials where calibration included linear and second degree polynomial fits to the standards when the intercept was constrained to zero.

An analysis of variance (F-test) using pure element standards showed that 34 out of 48 absolute errors for the Fe-Ni system using the three different compilations and bichromatic excitation were significantly different at confidence levels ranging from 90 to 99%. The degree of agreement between results with the different compilations improved with "type" standards where, with linear calibrations only, 14 out of 48 absolute errors were significantly different, and with a second degree polymonial fit, no significant differences were observed.

It was concluded from this work that, for some sample types, different mass absorption coefficient compilations can lead to serious differences in results, especially when only pure elements or no standards are used for calibration. In regions where serious differences occur, more good experimental measurements may be needed to resolve disagreements.

11. XRF Analysis of Marine Sediments (NOAA/NBS Specimen Bank) by Automated Borate Fusion

G.A. Sleater

A new class of materials that was analyzed by XRF spectrometry in the past year consisted of marine sediments. Six samples of marine sediments were taken from materials stored in the National Environmental Bank at NBS; four samples were supplied by NOAA. The analyses, done for the Specimen Bank, were intended not only to determine the composition of the sediments but also to furnish information for selecting future Standard Reference Materials.

The ten samples varied in consistency from fine, flour-like powders to gritty, sand-like materials. As the analytical specimens were to be prepared from the samples by automated fusion with a lithium tetraborate flux at 1050 °C to form homogeneous glass disks, preliminary studies were made to determine the loss on ignition (LOI) of each sample at this temperature. Because the range of LOIs was so great (from about 1% to 55%), all sample materials were pre-ignited at the above temperature before preparing the fused specimens; this pre-ignition ensured a uniform ratio between sample and flux in all specimens.

To determine concentrations from XRF intensity data, synthetic standards containing the elements of interest were prepared from high purity (99.999%) reagents under conditions identical to the preparation of the marine sediment specimens. Preliminary concentrations for the sediments were calculated using the NBSGSC fundamental parameter program for interelement corrections developed in this Group. Additional synthetic standards were then prepared to duplicate the concentrations calculated for each marine sediment sample, and final concentrations were calculated.

The concentration ranges (weight percent) for the ten elements determined by XRF spectrometry are given below. Wavelength-dispersive spectrometry was used to determine all concentrations, except for Rb and Sr which were measured by energy-dispersive XRF analysis.

Si: (36.69% - 12.87%)
Al: (7.84% - 3.72%)
Fe: (5.22% - 1.41%)
K: (2.27% - 0.61%)
Ca: (1.97% - 0.28%)
Ti: (0.63% - 0.21%)
Mn: (0.12% - 0.027%)
Zn: (0.023% - 0.0012%)
Sr: (0.040% - 0.011%)
Rb: (0.013% - 0.0016%)

12. Determination of Absorption and Pressure-Broadening Coefficients for Selected Infrared Transitions of NO_2 by Tunable Diode Laser Absorption Spectrometry

A. Fried and R.L. Sams

The reactive gas NO_2 is one of many key atmospheric species presently being studied worldwide in numerous laboratories as well as in the ambient environment. To meet the ensuing need for accurate standards employed in these various studies, the National Bureau of Standards has been actively involved in providing and certifying NO_2 standards capable of delivering concentrations in both the parts-per-billion (ppb) and parts-per-million (ppm) ranges.

As part of our long-term program to ensure high accuracy in such calibration standards, the Analytical Laser Spectrometry Group has been active in developing alternate methods by which to verify calibration. Tunable diode laser absorption spectrometry (TDLAS) is a particularly attractive means to accomplish this in both of the above mentioned concentration regimes. However, accurate molecular parameters, such as absorption and pressure-broadening coefficients must first be determined. The present study was therefore undertaken with this goal in mind.

Traditionally, absorption coefficients for NO_2 have been determined only using pressure measurements to derive the number-density of the absorbing species. Because of the presence of N_2O_4 and the reactive nature of NO_2, systematically low absorption coefficient results are likely to occur employing pure samples of NO_2, unless special precautions are taken. To address this problem, a novel approach was developed which completely eliminated the possibility of such sources of error. This was achieved by utilizing dynamically generated NO_2 permeation standards in the 50-100 ppm range employing specially prepared permeation tubes. In this way, the IR absorption cell was continuously exposed to fresh sample gas. More importantly, this approach enabled us to determine the concentration of the sample gas with a great deal of redundancy. We first utilized the conventional gravimetric approach in which the sample gas concentration was determined based upon accurate flow calibrations and permeation tube weight loss measurements. Fourier transform IR spectrometry (FT-IR) was next employed to search for impurity gases like HNO_3 co-permeating with NO_2. No other gases were found. The accuracy of the gravimetric determination was further corroborated by integrated band absorption measurements employing FT-IR as well as by gas phase titration, as will be thoroughly discussed in a subsequent report.

Employing such unprecedented redundancy in determining the sample gas concentration, absorption and pressure-broadening coefficients for over 26 of some of the stronger IR absorption lines of NO_2 (6.2 μm spectral region) were determined. As a result of this effort, TDLAS can now be employed with high accuracy to measure NO_2 standards independently.

13. Construction and Characterization of a Highly Accurate Dynamic NO_2 Calibration System for NASA's Global Tropospheric Experiment

A. Fried, L. Nunnermacker, B. Cadoff, N. Yates, R. Dickerson, R. Sams, and J. Norris

The National Aeronautics and Space Administration (NASA) is sponsoring a multi-year program to study the non-urban troposphere, the Global Tropospheric Experiment (GTE). In the second phase of this study scheduled for August 1986, important atmospheric constituents such as NO_2 and HNO_3 will be measured at trace background levels extending down well below one part-per-billion (ppb). Accurate calibration standards in this concentration range are therefore required.

Because of our expertise in trace NO_2 standards, the Analytical Spectrometry Group was asked by NASA this past year to construct and characterize a highly accurate dynamic NO_2 calibration system for use in this field experiment. Such trace level calibration standards can conveniently be prepared using low level (1-50 ppm) compressed gas NO_2 mixtures in a dynamic dilution system. The accuracy of the resulting trace gas mixture will obviously be directly tied to the accuracy of the input gas. However, in addition to significant amounts of HNO_3 found in these cylinders, the stability of the NO_2 concentration in such compressed gas mixtures remains unknown. Consequently, we decided to develop a dynamic calibration system centered around an NO_2 permeation tube standard.

The NO_2 permeation calibration system was constructed by modifying a commercial unit. First, thermostated mass flow controllers were added for precise and accurate flow control. A second dilution stage was next added to generate NO_2 concentrations as low as 0.5 ppb. To achieve this, most of the flow from the first stage has to be vented and only a very small flow of approximately 0.1 L min^{-1} (where the standard conditions are 25 °C and 1 atm pressure) is allowed to entered the second stage for dilution with 10 L min^{-1} (where the standard conditions are 25 °C and 1 atm pressure) of air. Control of this flow into the second stage is accomplished by controlling the vent flow with a mass flow controller. In this way, the permeant gas directly enters the second stage without going through a mass flow controller. Thus, we avoid the attendant uncertainty of concentration losses. The downstream side of the vent flow controller, however, must be connected to a vacuum pump to satisfy the necessary pressure drop for flow control without pressurizing the entire upstream side of the system. Extensive tests have been performed to characterize both the linearity of the system from approximately 30 ppb down to 0.5 ppb as well as the absolute NO_2 output concentrations. Determinations of these concentrations over this range have been carried out based upon permeation tube flow and weight loss measurements and compared with those determined using an ultra-sensitive chemiluminescence detector calibrated by NO SRM standards and gas phase titration. Agreement was typically within 2%, thus indicating no significant NO_2 losses as well as good mixing dynamics.

14. Development of a HNO_3 Calibration System for Dynamic Standards in the Parts-Per-Million Concentration Range

L. Nunnermacker, R. Dickerson, and A. Fried

Nitric acid (HNO_3) is an important molecule in atmospheric studies. This species plays a key role in the nitrogen chemistry of the atmosphere and is directly linked to major concerns associated with acid precipitation. As with NO_2, accurate gas standards in both the parts-per-billion (ppb) and parts-per-million (ppm) concentration range are required for both laboratory and field studies.

Commercial HNO_3 permeation tubes can deliver ppm and ppb levels of this gas, and a gravimetric calibration can be obtained from the weight loss and the flow rate in much the same manner as for an NO_2 permeation tube. However, while NO_2 permeation tubes contain pure NO_2, the HNO_3 tubes contain a mixture of HNO_3 and H_2O. A constant boiling azeotropic mixture of HNO_3 and H_2O permeates through the walls and thus the resulting weight loss does not accurately reflect the HNO_3 concentration permeating. During this past year, a research study was initiated to characterize accurately the HNO_3 concentration from such permeation tubes using dynamic standards in the ppm and ppb range.

In collaboration with the University of Maryland, we have been studying the reaction between HCl and $AgNO_3$ to form HNO_3 gas and AgCl precipitate. In the 100 ppm concentration range, this reaction was found to generate quantitatively one molecule of HNO_3 in the gas phase for every HCl molecule flowing (50-100 $scm^3\ min^{-1}$) into the $AgNO_3$ reactor tube. The gas eluting from the reactor tube was passed into aqueous solution where the resulting NO_3 ion concentration was measured by ion chromatography (IC). Since 99.6% of the gas-phase HNO_3 was found to be trapped in the first of a series of such solutions, the aqueous NO_3 ion concentration is directly related to the gas-phase concentration of HNO_3 in the flowing gas stream. This gives a direct means of calibration. In most cases, residual Cl ion, which would be indicative of unreacted HCl, was not found in solution. We therefore plan to measure accurately the HCl cylinder concentration by tunable diode laser absorption spectrometry (TDLAS), a task in which we have considerable expertise, to obtain a second independent calibration of the gas-phase HNO_3 concentration.

Continued research on this calibration technique is planned for the coming year. In addition to extending the technique to the low ppm and ppb range, studies are planned to couple the above two calibration approaches with three additional approaches using 1) chemiluminescence detection employing nylon scrubbers, 2) direct absorption by TDLAS, and 3) direct absorption by Fourier transform IR spectrometry. The resulting HNO_3 calibration system, which will serve as a working standard for permeation tube studies, will have the utmost in calibration redundancy.

15. Re-Investigation of the Gas Phase Titration Reaction Between NO and O_3: Redetermination of the Absolute Cross Section of O_3 at 254 nm

A. Fried, B. Cadoff, L. Nunnermacker, R. Sams, A. Bass, and J. Norris

This past year, research was resumed on the investigation of the stoichiometry of the gas phase titration (GPT) reaction: $NO + O_3 = NO_2 + O_2$. This reaction, which we studied four years ago, is very important since it provides a mechanism by which standards for the first three constituents can be intercompared. Such intercomparison is an integral part of our group's long term goal to ensure high accuracy in gas calibration standards provided by NBS. In the case of NO and NO_2, NBS provides and certifies NO standard reference material (SRM) gas mixtures and NO_2 permeation tube standards, respectively. Measurements of O_3 are carried out employing ultraviolet (UV) absorption photometry using the 254 nm Hg line, and thus the standard employed is the absorption cross section at this wavelength. The study of the GPT reaction was re-initiated this past year in an effort to explain and minimize a 3.6% systematic bias previously found between measurements of O_3 and those for NO and NO_2. The latter two constituents were in agreement to better than 1%.

As in our past study, all three constituents were measured employing independent techniques. Significant improvements, however, in both the generation and measurement of O_3 as well as the measurement of NO_2 were incorporated in the present study. Measurements of O_3 were carried out employing one of the Standard Reference Ozone Photometers which is part of the NBS/EPA national monitoring network. This photometer was developed by Bass and Paur and described in a number of previous reports. In contrast to the long path O_3 photometer using in our previous GPT study, both the short and long term stability for the new photometer and O_3 generator were excellent. We also improved our measurement capability for NO_2 in terms of sensitivity and selectivity utilizing tunable diode laser absorption spectrometry (TDLAS). In our previous study, NO_2 measurements were carried out employing photoacoustic spectrometry (PAS). Although PAS is fairly selective, the extremely high selectivity of TDLAS is further required in GPT studies to unequivocally verify that the oxidation of NO does not proceed beyond NO_2.

Throughout this study, the measured O_3 concentration was found to be consistently lower than the concentration of either NO or NO_2 by 1 - 1.5%. Agreement for the latter two species was typically better than 0.5%, thus offering further verification for both the NO SRM and NO_2 permeation standards. Work is continuing on this project. However, our results to date suggest that the presently accepted value for the O_3 cross section may have to be lowered by 1-1.5%, in almost exact agreement with the recently obtained direct UV absorption measurements of Mauersberger.

16. Technical Accomplishments of a Three-Year NBS-DOE Program for the Development of Standards and Reference Methodology for CO_2 in Air

E.E. Hughes, I.L. Barnes, J. Elkins, R.C. Myers, P.A. Johnson, and W.L. Zielinski, Jr.

The long-term data record at Mauna Loa and other global sites has demonstrated that global atmospheric carbon dioxide (CO_2) levels have been increasing markedly over the past three decades, from 316 ppm in 1958 when continuous monitoring was initiated to 345-350 ppm in 1985. Such monitoring is needed to quantify accurately the temporal and long-term changes in atmospheric CO_2 to assess future impacts of these changes on global warming and climate. During this period, standards to calibrate continuous monitoring were provided by the Scripps Institution of Oceanography (SIO) at the University of California, La Jolla.

To ensure the long-term availability of CO_2 gas standards, an interagency research program having three basic components was established to institutionalize the availability of such standards at the National Bureau of Standards. These three research components were: (1) the development of highly accurate and stable CO_2 in air Standard Reference Materials (SRMs) over the 300-400 ppm range of interest; (2) a research evaluation of the equivalency of gravimetry (employed by NBS) and manometry (employed by SIO), and (3) the research development and evaluation of a second reference method at NBS to independently confirm NBS gravimetric values for the future (isotope-dilution mass spectrometry [ID-MS]).

This program has led to the development of seven batches of stable SRM's for CO_2 in air having a 95% concentration uncertainty not exceeding 0.1% relative, covering the important range of 330-380 ppm (nominally at 330, 340, 350, and 370 ppm). Additional SRM's are in process or planning for 300 and 360 ppm, with wider range standards (at 200 and 1000 ppm) for agriculture research on CO_2 effects. Intercomparison studies between NBS and SIO revealed some slight differences (which appear to be resolvable) and generally excellent agreement in CO_2 concentrations determined in identical standards, the results of which confirm that the use of NBS SRM's will ensure the long-term scientific continuity of the existing monitoring data record. Finally, a computer-controlled ID-MS system has been completed and currently is under final evaluation for accurate CO_2 measurements in NBS SRM's. The ID-MS system is based on the use of three Faraday cups to simultaneously collect signals at m/e 44, 45, and 46, and the use of a computer program to collect and deconvolute the data.

A detailed report describing the activities and accomplishments of the three separate components of this program has been published for world-wide distribution to researchers and programs involved in carbon dioxide research ("High Accuracy Standards and Reference Methodology for Carbon Dioxide in Air," Report No. TR033, DOE/PR-06010, June 1986). This joint report of DOE's Carbon Dioxide Research Division and NBS' Center for Analytical Chemistry is available from the National Technical Information Service, Springfield, VA 22161.

17. Assessment of the Air Matrix Effect in the Non-Dispersive Infrared Analysis of CO_2 in Air Standards

R.C. Myers, E.E. Hughes, and W.L. Zielinski, Jr.

Global programs for monitoring the atmospheric level of carbon dioxide (CO_2) and its change over time rely on data generated by a non-dispersive infrared (NDIR) analyzer that is specific for CO_2. Such analyzers have routinely been calibrated by the use of standards of CO_2 in a nitrogen or air matrix. It has long been established, however, that a CO_2 in air standard will produce an NDIR signal that is lower than that produced from a standard containing the same concentration of CO_2 in nitrogen. This matrix effect results in an error in the order of 4 ppm for air. The effect is caused by a pressure-broadening of the CO_2 response by oxygen (in a CO_2-in-air matrix), resulting in a decrease in the amplitude of the response relative to nitrogen.

To further complicate this issue, argon (present in real air) also decreases the NDIR signal. On an absolute basis, preliminary results indicate that the argon effect may be greater than that of oxygen; however, on a real air basis the argon and oxygen effects appear to be of the same magnitude, and may, to a first approximation, be additive. To illustrate, if one compares the NDIR signal for three standards having the same CO_2 concentration, one in pure nitrogen, one in pure oxygen, and one in pure argon, the signal for the oxygen and argon standards are approximately 19 and 25 ppm lower, respectively, than that obtained for the nitrogen standard. However, since real air has a composition of 21% oxygen, 0.93% argon, and 78% nitrogen, the NDIR air matrix effect for a 1% difference in argon and oxygen is in the order of 0.25 and 0.2 ppm, respectively. These effects emphasize the importance of knowing the matrix composition of the standards being used to calibrate NDIR equipment for accurate measurements of atmospheric CO_2. The use of calibration standards that contain no argon may result in an error in the order of 0.2 ppm; using standards that contain only nitrogen may result in an error in the order of 4 ppm; using different standards of CO_2 in air that contain varying matrix compositions may result in a data scatter that would be difficult to interpret if such compositional differences are unknown or appropriate corrections for matrix differences are not applied. Since researchers involved in global monitoring of atmospheric CO_2 routinely report their data to at least the nearest 0.1 ppm and are extremely interested in detecting subtle seasonal changes in atmospheric CO_2, accurate calibration of NDIR analyzers is essential. To quantitatively correct NDIR responses for differences in the air composition of CO_2 in air standards, the exact effects must be known and be predictable for changes in the composition of the air matrix. Research is currently being extended in this area to further this understanding and predictability. The results of this research should be directly extendable on a relative basis to other NDIR analyzers used by the atmospheric CO_2 research and monitoring community.

18. Assessment of the Absolute Error in the Use of Primary Gravimetric Standards for the Development of CO_2 Air SRMs for Global Monitoring of Atmospheric CO_2 Changes

E.E. Hughes, J. Elkins, R.C. Myers, H.L. Rook, and W.L. Zielinski, Jr.

The certification of gaseous SRMs involves (a) the preparation of primary gravimetric standards bracketing the concentration range of the gas mixture in a homogeneous batch of approximately 50 cylinders, (b) the assignment of concentration of the gas mixture in a sample taken at random from the batch ("batch standard") by analytical intercomparison with the primary standards, and (c) the assignment of certified concentrations to the remaining samples in the batch by analytical intercomparison with the batch standard. The total uncertainty (at 95% confidence) assigned to the certified concentration is estimated by summing, in quadrature, the total error due to preparation of the gravimetric primary standards and the errors associated with the two principal analysis steps. The analytical uncertainties are determined directly from the analytical data; the assessment of the error in the primary gravimetric standards, hence, represents a critical control point in the overall certification process.

In the case of CO_2-in-air SRMs, the two analytical errors are of the same magnitude, and each are in the order of 0.02-0.05 ppm. To assess the error in the preparation of the primary gravimetric standards, one must sum the individual component errors due to the preparation steps. These errors include: the errors in the weights used in weighing the pure CO_2 and air reagents; the weighing imprecision; the measurement of the purity of the CO_2; the molecular weight determined by careful analysis of major and minor components of the air reagent; and any transfer errors associated with the transfer of the reagents into the pre-weighed, evaluated primary cylinder. The random error comprising these individual errors can be assessed by determining the difference between gravimetrically-calculated concentrations and concentrations obtained from a parabolic regression of the gravimetric concentrations against voltages obtained by high-precision non-dispersive infrared (NDIR) analysis. Independent intercomparisons with another absolute method for CO_2 (manometry) have indicated the absence of a large systematic error in the gravimetric procedure.

Research studies were carried out recently to verify the internal consistency of sets of primary gravimetric standards for CO_2-in-air by regressing NDIR signals against gravimetric concentrations over a range of 270-410 ppm. In addition, research was carried out to intercompare the gravimetric method with an alternative gravimetric method involving the intermediate preparation of a 1.5% CO_2-in-air primary standard from which gravimetric primaries in the 270-410 ppm range were directly prepared. This alternative method ("double-dilution") produced primaries having an apparently greater internal consistency than the standard method (i.e., lower mean residuals between gravimetric and NDIR-correlation values). This second method was evaluated since it had been determined that the largest individual error in the gravimetric procedure was due to weighing and a greater weight of CO_2 reagent could be used in this method. Current results indicate that it is feasible to prepare a set of primary gravimetric standards for CO_2-in-air with a total uncertainty on the order of 0.1 ppm or less. Long-term analyses (over 5 years) have shown primary standards and SRM's to be stable.

19. Characterization of the Temperature Dependence of the Infrared Band Strengths of Halocarbons F-11 (CCl_3F) and F-12 (CCl_2F_2) Using a Cryogenic Gas Cell and FT-IR Spectrometry

J. Elkins and R. Sams

Halocarbons F-11 (CCl_3F) and F-12 (CCl_2F_2) have strong absorption bands in the infrared "atmospheric window" for the absorption of terrestrially-irradiated infrared (IR) energy. Releases of these halocarbons into the atmosphere from anthropogenic activities may increase the surface temperature of the earth ("greenhouse effect"). Band strength measurements can be obtained by FT-IR analysis; such measurements relate the amount of IR radiation absorbed per molecule, which is important in calculating the radiative budget of the atmosphere. Few such measurements exist for these halocarbons at room temperature; even fewer results are available at the lower temperatures that are representative of those in the upper atmosphere.

Research was carried out using an FT-IR spectrometer and a specially-designed cryogenic gas cell to measure the band strengths of these halocarbons in the atmospheric window between 8 and 16 microns at a resolution of 0.06 cm^{-1}, at three temperatures: 297, 273, and 238 K. The cryogenic cell was a cylindrical stainless-steel cell having a vacuum maintained between two walls (for insulation); temperature-controlled by circulated, refrigerated ethanol; three platinum resistance thermometers and CsI internal and KBr external windows. The cell temperature was maintained to within 1 K at 297 and 273 K, and to within 2 K at 238 K.

The band strengths were found to be constant within experimental error over the range of temperatures studied. The shape of the bands, however, showed a temperature dependence, being narrower and of higher amplitude with decreasing temperature. Specific band strengths were determined for halocarbon F-11 in three principal IR ranges (760-880, 1020-1120, and 900-960 cm^{-1}), and for halocarbon F-12 in two ranges (855-950 and 1050-1200 cm^{-1}). These results should be of interest to atmospheric scientists concerned with accurate measurements of these halocarbons in the atmosphere, and show a temperature dependence when using absorptivities based on band amplitude but not on band area (i.e., band strength).

20. Development of a Seventeen-Component NBS-Traceable Volatile Toxic Organic Gas Standard at 10 ppb for GC-MS Calibrations

G.C. Rhoderick and W.L. Zielinski, Jr.

Analyses of ambient air samples for volatile toxic organic compounds are routinely conducted using 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 was conducted at NBS to assess the feasibility of developing a gas standard containing a substantial number of these compounds.

The mixture was compounded by initially preparing two eight-component mixtures using a microgravimetric procedure established here. One of the pure organics was quantitatively introduced into a pre-weighed evacuated cylinder by the standard microgravimetric procedure. Following this, a pre-calculated amount of each of the two eight-component mixtures was transferred to the same cylinder, which was then pressurized with a pre-calculated amount of pure nitrogen gas (the matrix). The resulting mixture contained the following organics:

bromoethane
chloroform
1,2-dichloroethane
1,1,1-trichloroethane
trichloroethylene
1,2-dibromoethane
toluene
ethylbenzene
<u>o</u>-xylene
vinyl chloride monomer
trichlorofluoromethane (F-11)
carbon tetrachloride
1,2-dichloropropane
benzene
tetrachloroethylene
chlorobenzene
styrene

The concentrations of the individual organics were determined by analytical intercomparisons with primary gravimetric standards that had been independently verified for accuracy. Analyses were carried out by gas chromatography using a linear temperature program (45 °C for 3 minutes, followed by a 8 °C/min increase to 220 °C), a column of 1% SP-1000 on 60-80 mesh Carbopack B, a N_2 carrier gas flow of 30 mL/min, a gas sampling valve and loop, and flame-ionization and electron-capture detection.

This standard represents the most complex, stable, ppb concentration calibration mixture ever prepared. The standard was developed under an NBS-EPA interagency program for EPA/EMSL/RTP, and has already been used for calibrating GC-MS analyses of field samples taken from a major industrial area.

21. <u>Development of NBS-Traceable Gas Standards to 1 ppb for Dry Acid Deposition Studies</u>

W.D. Dorko and Z.T. Cai

Meaningful measurements to study dry acid precipitation require characterized gas standards for acidic molecules at the 1 ppb level, the major compounds being SO_2, NO and NO_2. The most useful type of standard is a compressed gas mixture contained in a high pressure cylinder. However, there are no cylinder standards available at this level for either of the three mentioned gases. These gases exhibit reactive and corrosive properties, therefore, special precautions are required when trying to prepare stable gas mixtures of them at any concentration and the difficulties increase as the concentration levels decrease.

The next most convenient method for providing gas calibration standards is by dynamic dilution, where the final mixture flows from a blending process rather than from a contained static mixture. The input for the gas of interest can be a permeation device (if appropriate) or a higher concentration cylinder mixture. Due to practical limitations in the maximum dilution ratio (generally, about 100:1) low concentration inputs to the dilution system must be used to attain an output concentration of 1 ppb. In this program, specially prepared cylinder mixtures containing nominal concentrations of either 100 ppb, SO_2 or NO were evaluated for long-term stability. A dynamic dilution system consisting of in-house calibrated mass flow controllers was rigorously characterized using inputs either from thermostatically controlled SO_2 and NO_2 permeation tubes or from higher concentration cylinder mixtures of SO_2 and NO, and appropriate detectors. The 100 ppb cylinder mixtures are then used as inputs to the dilution system to produce calibrating mixtures ranging down to 1 ppb. At these low concentration levels, however, background levels of the gaseous analytes of interest in the dilution gas itself can represent a serious problem. Sulfur dioxide may be removed by scrubbing, therefore several materials were tested and the best one chosen as a scrubbing agent through which the air is passed to provide both a zero and dynamic dilution diluent gas. Nitric oxide is not easily removed by scrubbing, and therefore, the "zero" gas is reacted with O_3 to convert any NO to NO_2 before entering the NO detector. An evaluation of the other possible sources of systematic error, including reaction of the gaseous specie of interest with the transfer lines and flow controllers prior to dilution, was found not to exceed 1.5% relative.

The characterized 100:1 dynamic dilution system and an NBS-traceable, stable compressed gas cylinder standard containing 100 ppb SO_2 in air have been delivered to EPA for dry acid deposition studies. Similar standards for NO and NO_2 are in progress.

22. Comparison of Single-Component Standards to Multi-Component Standards for Use in the Analysis of Natural Gas

G.C. Rhoderick and E.E. Hughes

Precise compositional analysis of natural gas mixtures requires that specific quantifications be made for each of the components present in such mixtures. Since the natural gas industry has been in the process of changing from billing customers by volume to billing by BTU and is evaluating the feasibility and reliability of changing from traditional calorimetric determinations of BTU to compositional gas chromatographic determinations of BTU, precise compositional analyses have become critically important. Errors associated with such analyses can have a substantial economic impact, considering the huge volume of natural gas consumed annually. Precise compositional analyses of natural gas standards have been provided for national calibrations by the Center for Analytical Chemistry for many years, with the most recent ones provided in 1985. The resultant NBS-traceable compositional standards are subsequently used to characterize natural gas secondary standards that are used throughout the U.S. to provide data quality assurance in the production of natural gas by the natural gas industry.

Single- and multi-component primary gravimetric standards prepared by NBS are used for the compositional characterization of NBS-traceable natural gas standards. The error associated with the use of both single- and multi-component standards had not previously been evaluated. While multi-component primary standards may simulate the composition of natural gas mixtures being analyzed, the preparation of single-component primary gravimetric mixtures is simpler. Research studies were carried out to assess the relative error in using single-component and multi-component primary gravimetric standards.

Several simulated natural gas mixtures containing methane, seven higher hydrocarbons, nitrogen, and carbon dioxide were obtained. Concentrations of the components of these mixtures were determined from gas chromatographic calibrations using multi-component primary gravimetric standards (containing all of the components of these mixtures) and from similar calibrations using single-component primary gravimetric standards (containing different concentrations for each component in a methane matrix). The total concentration uncertainty (95% confidence) of the individual components in the primary standards did not exceed 0.5% relative.

The differences in the concentrations of the components of the mixtures, obtained from the two types of calibrations, were small when the total differences for all mixture components were considered. The difference in the concentrations of the non-methane hydrocarbons in the mixtures between the single-and multi-component calibrations ranged from 0.02% relative (for ethane at 4 mole-%) to 1.2% relative (for ISO-pentane at 0.1 mole-%); however, these differences were within the analytical imprecision, demonstrating that no real difference existed using calibrations with single- vs. multi-component standards. Gas chromatographic analyses of methane revealed a slight decrease (1.0%) in the methane response factor (peak area divided by concentration) when identical sample sizes taken from pure methane (100%) and a series of primary standards ranging down to 75% methane. Since methane is the main contributor to the BTU value of natural gas mixtures, this finding emphasizes the importance of using a methane standard that has a methane concentration quite similar to that in the mixture being analyzed.

The effect of the total differences obtained from calibrations using single- vs. multi-component primary standards on the heating value of analyzed natural gas mixtures was only 0.2 BTU, which is well within the typical uncertainty of 1 BTU for a natural gas sample. This research indicates that carefully prepared single-component standards may be used in place of multi-component standards in precise compositional analyses of natural gas mixtures.

23. <u>Technical Up-Grade of Analytical Gas Mass Spectrometer</u>

W.D. Dorko and E.E. Hughes

The Gas Metrology Group's gas mass spectrometer (a CEC 21-103-C) was installed in 1961. It is a magnetic sector instrument with a Faraday cup detector which has excellent linear response characteristics over a wide concentration range. It also is equipped with a batch inlet system for direct entry of pure gases, gas mixtures, or volatile liquids. This instrument plays a key role in the Group's research and development activities in the preparation and evaluation of primary gas standards for the certification of gaseous SRMs. It is used in the purity assay of reagent gases and as one of several techniques for verifying major and/or minor components in the final gas mixtures. It also is used frequently as the primary analytical technique, in a variety of other agency, university, and industrial projects. The Division's Atmospheric Chemistry Group has modified part of the instrument for use in determining the CO and CO_2 in gas samples produced by the oxidation of very small amounts of atmospheric carbonaceous material.

Over the past years, a number of the original components of this system have been replaced with components of improved technology. However, the system's three main circuits (ionization region control circuit (isotron), high voltage power supply circuit, and magnet power supply and control circuit) remained. These utilize 1950's technology involving vacuum tubes, which often are difficult to obtain. Furthermore, these circuits were aging to the point that the overall performance was frequently marginal and unpredictable.

During 1986, these three vacuum tube-based circuits were replaced with specially designed solid-state modules that incorporate modern technology. The design of these modules was developed as a single purchase package, such that the connection of a module to other modules or to other components of the mass spectrometer was accomplished with cables and connectors without hard-wiring. This allows great flexibility in configuring the system and an efficient use of space.

The up-graded mass spectrometer now is operating better than it did when it was first acquired in 1961. Its performance is excellent, stable, predictable, and more versatile. Projects that require isotope quantitation can now have data generated by magnetic scanning instead of by electrostatic scanning. The magnetic scan provides better quantification and statistics due to a new capability for unattended, automatic magnetic up-field and down-field scanning. The electrostatic and magnetic mass scanning rate can be linearly adjusted from very fast to very slow. This allows for a very rapid qualitative survey scan of an unknown sample, or for the development of quantitative data at slower rates. The ultimate instrument resolution (e.g., separate D_2 from He) can be achieved by using even slower rates. In addition, the accelerating voltage and magnetic field strength (using a new Hall probe) can be read accurately from the front panel for calculating fragment mass numbers for identifying unknown sample components.

In summary, the up-graded mass spectrometer not only exceeds its original performance specifications, but now contains useful features that were not originally included.

24. Chemometrics: National and International Activities Related to Nomenclature, Detection, and Reporting of Analytical Data

L.A. Currie

During the past year, significant efforts have been devoted to central issues related to the performance characteristics of the Chemical Measurement Process (CMP). The primary channels through which these efforts have taken place were the Quality Assurance Task Force (QATF) of the Center for Analytical Chemistry, the International Union of Pure and Applied Chemistry (IUPAC), the International Atomic Energy Agency (IAEA), and the American Chemical Society (ACS). Besides these four rather intensive activities, which will be described below, requested guidance on the treatment of detection limits and analytical uncertainties has been given to nuclear power industry personnel, an American National Standards Institute committee developing performance criteria for radiobioassay, and an NBS working group on the expression of measurement uncertainties. This last group is charged with framing NBS inputs for international efforts through the International Standards Organization.

Work performed as a member of the QATF included the development of a draft document, "Guidelines for Characterizing the Chemical Measurement Process and the Reporting of Analytical Results." Primary cooperation in this effort was given by the other two subcommittee members, J.K. Taylor (550) and R. Zeisler (551). The document presents recommendations concerning many issues arising in the characterization of the CMP, ranging from definitions of the principal performance characteristics, to means for estimating them on the basis of statistical approaches as well as chemical knowledge, to recommendations for control, treatment of multicomponent data, and the reporting of results. A summary table is included, containing symbols, terminology, references, and estimation and reporting guidelines.

In parallel with the QATF activity was work for the IUPAC Commission on Analytical Nomenclature. Final work is underway on reports to the Commission entitled "Recommendations for Nomenclature in Evaluations of Analytical Methods" and "Recommendations for the Presentation of Results of Chemical Analysis." The latter effort is being carried out in cooperation with G. Svehla, former Chairman of the Commission, who prepared the initial drafts.

The IAEA has developed special needs in the area of detection limits, in connection with its international comparison program and its coordinated research programs involving trace analytical measurements in bioenvironmental matrices. As a result, a special Consultants Meeting on the Limit of Detection (LOD) was held last December at IAEA headquarters, where Agency scientists headed by R.M. Parr plus five international experts met to address the problem and draft a report or manual to be used in the Agency programs. The difficulties treated were manifold. Results of intercomparisons showed, for example, that diverse terminology and numerical expressions for the LOD were in use. More serious, however, was the fact that totally inconsistent results were being reported: in some cases trace elements were reported by some laboratories at orders of magnitude higher concentrations than the detection limits of other laboratories which reported "none detected." A primary focus for the manual which is in preparation is to force attention to measurement quality in the region of the LOD, especially through rigorous control of matrix corrections and realistic assessment of the blank.

A Symposium on "Detection Limits: from Basic Concepts to Practical Applications," was organized at the invitation of the Analytical Division of the ACS for the spring meeting in New York in April 1986. The two day, four session meeting treated the topic from quite a broad perspective. All papers were invited, and they ranged from fundamental statistical concepts and fundamental chemical limitations to public policy issues, and important applications in clinical, geo-, forensic, and environmental chemistry. A symposium volume, to be published by the ACS, is now in preparation. It will contain two chapters by L.A. Currie, one consisting of an overview of the evolution and importance of the concept; the other, summarizing approaches developed for the special radioactivity monitoring needs of the Nuclear Regulatory Commission and the forementioned bioenvironmental trace analysis requirements of the IAEA.

25. Microchemical and Isotopic Carbon: Accuracy, Precision and Applicabilities of an Improved Measurement Process Coupled to Accelerator Mass Spectrometry

R.M. Verkouteren and L.A. Currie

The abundance of the naturally-occurring radioisotope ^{14}C in carbonaceous materials reflects the systematics behind carbon cycle geochemistry, receptor modelling, and the chronology of natural and anthropogenic artifacts. Of particular interest are radiocarbon abundances in samples containing only very small amounts of total carbon (< 100 μg); e.g., specific chemical subfractions in atmospheric air and aerosol samples, amino acid fractions from ancient bones, and carbonaceous particles from glaciers and ice sheets. When extracted from a contaminated host matrix, separated fractions should give reliable radiocarbon values.

Samples are processed in a closed system to prevent atmospheric contact, hence minimizing that source of contamination and avoiding many operator dependencies. Gaseous or particulate samples are thermally and/or chemically processed to separate and purify the carbonaceous species of interest, then combusted to CO_2 and cryotransferred to a reduction tube where elemental carbon is deposited on an iron wool catalyst at 600 °C. Complete reduction, monitored by recording the pressure drop and confirmed by gas chromatography of the residual gas mixture, is achieved within twelve hours. Total carbon analysis by LECO of the iron wool blanks indicates 0.4 ± 0.5 μg C per target disc.

To assess the accuracy, precision and applicabilities of this measurement process, targets were generated containing from 50 to 990 micrograms of carbon. Carbon-12 ion currents were measured and found to be sufficiently intense (from 5-70% those of pure graphite) to enable beam focusing and to give statistically meaningful count rates. With 100 micrograms of "dead" carbon, the ^{14}C blank was 0.006 f_M (fraction of modern level); 600 micrograms of "dead" carbon gave $f_M < 0.001$ (> 43,000 yr BP). Measurement of NBS oxalic acid containing 550 µg C gave $f_M = 1.339 \pm 0.028$, within one standard deviation of the true value, and indicating a measurement imprecision of 2.1% (RSD). In progress is an assessment of accuracy and precision for measurements of smaller samples, as well as samples diluted with isotopically pure $^{12}CO_2$ to larger size.

In conjunction with carbon isotopic measurements of small samples, radiocarbon enhancement via thermal (hot wire) diffusion of CO is being pursued. Computer simulations of microchemical diffusion in the column at the NBS indicate a maximum ^{14}C enhancement of 300-500x in 1-2 months, corresponding to an increase in the conventional radiocarbon dating limit by about 40,000 years. Investigations into the effect of ternary mixtures (CO + N_2) on radiocarbon enhancement factors are also planned. An important and interesting by-product of this research will be the ability to study the rare terrestrial nuclear reactions, *per se*, thus possibly gaining knowledge of "paleo" neutron fluxes in geological and glaciological contexts.

26. ^{14}C in Elemental Carbon and Trace Organics: The Integrated Air Cancer Project

G.A. Klouda, A.E. Sheffield, and L.A. Currie

This year's activities, related to the chemical and isotopic (^{14}C) composition of urban atmospheric carbonaceous particles, involved participation in EPA's Integrated Air Cancer Project (IACP). The purpose of the IACP was to identify the chemical constituents, biological activity, and isotopic composition of the fine particles collected during the winter of 1984 and 1985 in Raleigh, North Carolina and Albuquerque, New Mexico. The amount of elemental (non-volatile or soot) and organic (semi-volatile) carbon extractable from the fine particles in addition to their ^{14}C abundance was proposed for tracing mobile (fossil, $^{14}C = 0$) vs residential (wood burning) combustion sources contributing to winter time pollution episodes. Radiocarbon measurements of these carbon fractions and PAH extracts are valuable inputs to the receptor model for source apportionment. Also, ^{14}C measurement and AMES mutagenic bioassay of the bulk organic material would yield the origin of this biologically active or inactive material; important for human health reasons.

Our specific role was to develop and validate a thermal or chemical method to separate organic (C_o) and elemental (C_e) carbon fractions from the total particulate material for quantitative determination and subsequent ^{14}C measurements. Work began by investigating thermal methods with important considerations given to 1) removal of artifact carbon, e.g., adsorbed atmospheric CO_2, 2) the prevention of "charring" (low temperature pyrolysis) of organics, and 3) the determination of carbonate carbon; all of which could potentially alter the true C_o and C_e ^{14}C abundances.

An initial experiment was performed to study artifact carbon by applying a vacuum extraction/thermal oxidation technique to a prefired blank quartz filter. Results showed that 2 µg/cm^2 of artifact carbon was adsorbed on the filter and that all of this carbon was removed by vacuum desorption. Future experiments related to artifact carbon will include determination of the adsorption per unit area of a known volatile compound on quartz fiber filter material and its vacuum/thermal desorption characteristics.

Thermal separation techniques investigated were applied to known organic compounds, mixtures of organic compounds and soot or graphite, and EPA IACP ambient samples. Clean (without charring) C_o/C_e separations and good yields (~95%) were obtained when these thermal techniques were applied to known compounds and mixtures. In contrast, thermal results of C_o and C_e from the ambient particles were significantly different than expected, suggesting problems with charring of organic carbon. In an attempt to resolve the question of charring, a wet oxidation technique (cf. Schultz, 1962) was applied at NBS to aliquots of the same filters to remove quantitatively organic carbon with HNO_3 and thermally oxidize and volumetrically determine the remaining carbon (C_e).

A comparison of thermal analysis and thermal/optical analysis (R. Cary) for separation of C_o and C_e was made and results indicate that as much as 20 to 30% of the total carbon chars at low temperature. The thermal/optical approach utilizes the optical transmission of the filter during thermal volatilization to correct for any charring of organic material. NBS C_e results by wet oxidation/thermal combustion correlated well with the thermal/optical method. These preliminary results suggest that charring may be difficult to avoid during the thermal process and that the wet oxidation treatment followed by thermal combustion of the residue may be the most reliable means for isolating C_e for ^{14}C measurements.

Carbonate carbon was determined on aliquots of the same IACP filters analyzed thermally for C_o and C_e. Samples were treated with hot phosphoric acid and the evolved CO_2 was measured volumetrically. For all filters analyzed, carbonate carbon was not detected above the system blank (~2 μg or equivalent to < 1 μg/cm^2) and, therefore, is not a significant influence on the thermal C_e fraction.

Initial ^{14}C results, determined primarily on total carbon to date, show Albuquerque, NM, fractions of contemporary (biogenic) carbon (f_C) to be 0.58 ± 0.06 for a daytime sample and 0.80 ± 0.03 for a nighttime sample. A Raleigh, NC, nighttime sample gave an f_C of 0.88 ± 0.04 (f_C = 1.00 for 100% biogenic carbon). The results indicate the major impact of woodburning at night in both cities during the winter.

C. Outputs and Interactions
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Pella, P. A., "Modern Trends in X-Ray Fluorescence Analysis," Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, Beijing, China, November 19, 1985.

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Simons, D. S., "Determination of the Half-Life of Re-187 by Laser Microprobe Spectrometry," Third International Laser Microprobe Mass Spectrometry Workshop, Antwerp, Belgium, August 26, 1986.

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Etz, E. S., "Stokes and anti-Stokes Fluorescence of Er(3+) in the Raman Spectra of Erbium Oxide and Erbium Glasses," 10th International Conference on Raman Spectroscopy (ICORS-10), University of Oregon, Eugene, OR, September 3, 1986.

Newbury, D. E., "Application of Digital SIMS Imaging to Light Element and Trace Element Mapping," Fifth International Conference on Secondary Ion Mass Spectrometry, Washington, D. C., October 1, 1986.

3. Committee Assignments

Harry Rook
Chairman, EPA Scientific Review Panel on Quality Assurance
Chairman, Office of Water Data Coordination, Committee 5F
Chairman, ASTM D-22.03 Sampling and Analysis of Ambient Atmospheres
Member, ASTM D-22 Sampling and Analysis of Atmospheres
Member, ASTM D-22.01 Quality Assurance
Member, IUPAC Commission V.3 (Analytical Nomenclature)

Arnold Bass
Member, ASTM D-22 Sampling and Analysis of Atmospheres
Member, ASTM D-22.01 Quality Assurance
Member, ASTM D-22.03 Sampling and Analysis of Ambient Atmospheres
Member, Ozone Science Guidance Committee, NESDZS

David Bright
Member, ASTM E-29 Particle Size Measurement
Member, ASTM E29.04 Liquid Particle Measurement

Lloyd Currie
Member, ASTM E10.05.02 Task Group
Member, CAC, Quality Assurance Task Force
Titular Member, IUPAC Commission on Analytical Nomenclature
Chairman, Consultant's Group, International Atomic Energy Agency, on Limit of Detection
Member, Interagency Workshop on the Future of Accelerator Mass Spectrometry in the U.S.A.
Member, University of Maryland Thesis Committee (A. E. Sheffield)
Member, Editorial Board, Journal of Chemometrics

William Dorko
Member, ASTM D-22 Sampling and Analysis of Atmospheres
Secretary, ASTM D22.03 Sampling and Analysis of Ambient Atmospheres

Edgar Etz
Member, ASTM D-22 Sampling and Analysis of Atmospheres

Alan Fried
Member, NASA's Science Team Committee for the Global Tropospheric Experiment
Member, University of Maryland Thesis Committee (L. Nunnermacker)

Ernest Hughes
Member, ISO/TC 158 Gas Analysis
Member, ISO/TC 158/SC-1 Methods for Preparation and Definition of Gas Mixtures for Calibration
Member, ISO/TC 159/SC-2 Analysis of Natural Gas

Robert Myklebust
Member, ASTM E-2 Emission Spectroscopy
Member, ASTM E-2.04 Standard Reference Materials

Dale Newbury
- Member, ASTM E-42 Surface Analysis
- Member, Journal of Microscopy, Editorial Review Board
- Member, Scanning, Editorial Review Board
- Member, J. Trace and Microprobe Techniques, Editorial Review Board
- Member, Journal of Electron Microscopy Techniques, Editorial Review Board

Peter Pella
- Member, ASTM E-2 Emission Spectroscopy
- Member, ASTM E-2.02 Statistics, Calibration and Standardization

Gerald Sleater
- Member, ASTM D-22 Sampling and Analysis of Atmospheres
- Member, ASTM D-22.06 Source Sampling

Walter Zielinski
- Member, Interagency Committee on CO_2 and Climate
- Member, Interagency Committee for Stratospheric Ozone Protection
- Member, Interagency Committee for Indoor Air Quality
- Member, ASTM D-22 Sampling and Analysis of Atmospheres
- Member, Journal of Analytical Toxicology, Editorial Review Board

4. <u>Others</u>

a. <u>Seminars</u>

November 13, 1985 - Professor D. J. Donahue, University of Arizona, "Application of Accelerator Mass Spectrometry to Some Problems in Archaeology and Geophysics." (Division Sponsor: L. Currie)

July 31, 1986 - Dr. Yohichi Gohshi, University of Tokyo, "X-Ray Fluorescence Analysis with Synchrotron Radiation." (Division Sponsor: P. Pella)

September 10, 1986 - Professor E. R. Malinowski, Stevens Institute of Technology, "Introduction to Factor Analysis in Analytical Chemistry." (Division Sponsor: L. Currie)

b. SRM Certification/Information Values

<u>Microanalysis</u>
- SRM 483, Homogeneity Testing and Compositional Analysis of Iron 3% Silicon Specimens
- SRM 1219, 431 Stainless Steel
- SRM 1223, 416 Stainless Steel
- SRM 1233, Valve Steel
- SRM 1250, CO Base High Temperature Alloy
- SRM 1761 - 1767, Low Alloy Steels Series

<u>X-Ray</u>
- SRM 1685B
- SRM 1686B
- SRM 1687B

SRM 2630
SRM 2631

Proposed SRM Brick Clay 679
Proposed SRM Dolomitic Limestone 88B

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 2627, 5 ppm Nitric Oxide in Nitrogen
SRM 2628, 10 ppm Nitric Oxide in Nitrogen
SRM 2629, 20 ppm Nitric Oxide in Nitrogen
SRM 1693, 50 ppm Sulfur Dioxide in Nitrogen
SRM 1694, 100 ppm Sulfur Dioxide in Nitrogen
SRM 2636, 250 ppm Carbon Monoxide in Nitrogen
SRM 2637, 2500 ppm Carbon Monoxide in Nitrogen
SRM 2638, 5000 ppm Carbon Monoxide in Nitrogen
SRM 2639, 1% Carbon Monoxide in Nitrogen
SRM 2642, 8% Carbon Monoxide in Nitrogen
SRM 1683, 50 ppm Nitric Oxide in Nitrogen
SRM 1684, 100 ppm Nitric Oxide in Nitrogen
SRM 2619, 0.5% Carbon Dioxide in Nitrogen
SRM 2621, 1.0% Carbon Dioxide in Nitrogen
SRM 2622, 2% Carbon Dioxide in Nitrogen
SRM 2624, 3% Carbon Dioxide in Nitrogen
SRM 2625, 3.5% Carbon Dioxide in Nitrogen
SRM 2626, 4.0% Carbon Dioxide in Nitrogen

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This report summarizes the technical activities of the Center for Analytical Chemistry at the National Bureau of Standards. It emphasizes activities over the Fiscal Year 1986 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; voluntary standards.

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