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**NBSIR 84-2979**

# **Technical Activities 1984**

## **Center for Analytical Chemistry**

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R. A. Velapoldi, H. S. Hertz, and J. K. Taylor

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

October 1984

Final

Issued December 1984

Prepared for  
**U.S. DEPARTMENT OF COMMERCE**  
National Bureau of Standards  
Gaithersburg, MD 20899

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**CENTER FOR ANALYTICAL CHEMISTRY**

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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

### 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 (SRM's). The ubiquity of and demand for analytical measurements in modern society is reflected in the diversity of SRM's produced in the Center. These reference materials are widely used in such diverse areas as the metal 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 - hazardous chemical and nuclear wastes, body fluids, plant and animal tissues, foods, 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 reference materials. As it is not reasonable to contemplate the development of SRM's to deal with every measurement problem, the Center's program must be multi-faceted, 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 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.

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

In an effort initiated in 1983, we are devoting considerable attention in the Center to better definition of our user communities and the various mechanisms for interacting with these communities. A major component of this interaction is the service the Center provides as a National Reference Laboratory. During the past year we have expanded these services; a few examples of these activities indicate the breadth of interactions which are involved. Members of the Center staff have prepared major quality assurance documents for the Nuclear Regulatory Commission (NRC) and the National Oceanic and Atmospheric Administration (NOAA) on Lower Limits of Detection and Generic Quality Assurance Guidelines for Marine Pollution Measurements, respectively. In a meeting with the Standards Steering Committee of the Health Industry Manufacturers' Association (HIMA) we discussed the NBS role as a scientific liaison for the regulatory and voluntary standards communities. In several meetings with members of the Compressed Gas Manufacturers Association, we discussed the traceability program for trace-level gas Certified Reference Materials (CRM's). We are currently preparing a document on the meaning of traceability to NBS chemical measurements, in general. Finally, NBS is playing expanded quality assurance roles in a Navy-sponsored organo-tin measurement program, a National Cancer Institute sponsored nutrient chemoprevention study, and an FDA-sponsored program on measurement of ethylene oxide residues. These latter measurements are of particular interest to, and our research was directly tied to, measurement programs of the American Institute for Medical Equipment Evaluation (an industry-sponsored consortium).

Directly related to our interactions with user communities is a major planning effort in chemical measurement services. As part of this activity, we are 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 late 1980's and early 1990's. 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 among the provision of currently needed standards and research efforts on new types of standards and methods of measurement. The work of the Center is performed in three divisions, each focusing upon specific sample types - 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 communities.

In the following, the major recent activities and technical directions of the divisions and groups mentioned above are summarized. Much work in progress is omitted but will be included in subsequent Annual Reports.

# 1. Outputs and Interactions

## a. Publications

Becker, D. A., "The Recycled Oil Program - Final Report", in NBS S. P. 662, U. S. Department of Commerce, National Bureau of Standards, Gaithersburg, MD 20899 (1983).

Becker, D. A., Hsu, S. M., and Weeks, S. J., "Lubricating Oil Basestock Data and Analysis: Based on the ASTM-NBS Basestock Consistency Study", Report DOE/BC/10749-2, U.S. Dept. of Energy, Washington, DC 20585 (Also published as NBS S.P. 661, 1983).

Gravatt, C. C., McClendon, L. T., and Hertz, H. S., "A Summary of Activities Related to Offshore Drilling of Petroleum at the National Bureau of Standards 1975-1981", Interagency Energy/Environment R & D Program Report (1983).

Hertz, H. S., Velapoldi, R. A., and Taylor, J. K., "Technical Activities 1983", Center for Analytical Chemistry, NBSIR 83-2786.

May, W. E., Brown-Thomas, J. M., Chesler, S. N., Guenther, F. R., Hilpert, L. R., Parris, R. M., Richie, K. L., Sonnefeld, W. J., Wise, S. A., and Hertz, H. S., "Interlaboratory Comparisons of Quantitative Analyses of Individual Compounds in Simple and Complex Mixtures", in Advanced Techniques in Synthetic Fuels Analysis, C. W. Wright, W. C. Weiner, and W. D. Felix, eds., Technical Information Center, U.S. Department of Energy, 381-404 (1983).

Taylor, J. K., "Reference Materials - What They Are and How They Should be Used," J. Testing and Evaluation 11, 355-7 (1983).

Becker, D. A., "Proceedings, Measurements and Standards for Recycled Oil - IV", NBS S.P. 674, U.S. Dept. of Commerce, National Bureau of Standards, Gaithersburg, MD 20899 (1984).

Becker, D. A., "Analysis for PCBs in Oil: The ASTM/NBS Round Robin", in Proceedings, Measurements and Standards for Recycled Oil - IV, NBS S.P. 674, U.S. Dept. of Commerce, National Bureau of Standards, Gaithersburg, MD 20899 (1984).

Becker, D. A. and Hsu, S., "NBS Provisional Tests for Re-refined Engine Oil", in Proceedings, Measurements and Standards for Recycled Oil - IV, NBS S.P. 674, U.S. Dept. of Commerce, National Bureau of Standards, Gaithersburg, MD 20899 (1984).

Becker, D. A., "The ASTM/NBS Basestock Consistency Study", in Proceedings, Measurements and Standards for Recycled Oil - IV, NBS S.P. 674, U.S. Dept. of Commerce, National Bureau of Standards, Gaithersburg, MD 20899 (1984).

Hertz, H. S., "SRM's and Definitive Methods: What are Their Roles in Accurate Clinical Measurements?", Pathologist XXXXVIII (5), 305-306 (1984).

- May, W. E., Chesler, S. N., Hilpert, L.R., Hertz, H. S., Rebbert, R. E. Vogt, C. R. and Wise, S. A., "Characterization of Polycyclic Aromatic Hydrocarbons in Air Particulate Extracts by Liquid and Gas Chromatographic Methods", in Identification and Analysis of Organic Pollutants in Air, L. R. Keith, ed., Butterworth Publications, Woburn, MA, 197-229 (1984).
- Taylor, J. K., "The Rising Interest in Quality Assurance", TRAC 3, No. 4, 2-6 (1984).
- Taylor, J. K., "Limits of Detection", Anal. Chem. 56, 130A (1984).
- Taylor, J. K., B. Kratochvil, and D. Wallace, "Sampling for Chemical Analysis", Anal. Chem. 56, 113R-129R April (1984).
- Taylor, J. K., "Guidelines for Evaluating the Blank Correction, "Testing and Evaluation 12, 54-55 (1984).
- Taylor, J. K., "Essential Features of a Laboratory Quality Assurance Program," Statistics in the Environmental Sciences, ASTM STP845, pp. 66-73 (1984).
- Taylor, J. K., "What is Quality Assurance?", in Proceedings of Conference on Quality Assurance of Environmental Monitoring", ASTM STP 867 (1984).
- Welch, M. J., Cohen, A., Hertz, H. S., Ruegg, F. C., Schaffer, R., Sniegowski, L. T., and White, V. E., "Determination of Serum Urea by Isotope Dilution Mass Spectrometry as a Candidate Definitive Method", Anal. Chem. 56, 713-719 (1984).
- Becker, D. A., and Hsu, S., "The NBS Recycled Oil Program: 1976 to 1983", in Proceedings, Fifth International Conference on Used Oil Recovery and Reuse, publ. by Association of Petroleum Re-refiners, Washington, DC 20006 (in press).
- Becker, D. A., "Quality Assurance Techniques for Activation Analysis," in Proceedings, Fifth International Conference on Nuclear Methods in Environmental and Energy Research, U.S. Dept. of Energy, Report XXX, Washington, DC 20585 (in press).
- Hertz, H.S., Wolf, W. R., "Open Discussion On Needs and Uses for Biological Reference Materials", in Biological Reference Materials Availability, Uses, and Need for Validation of Nutrient Measurement, W. R. Wolf, ed., John Wiley and Sons, Inc. New York, NY (in press).
- Velapoldi, R. A., Hertz, H. S., "The Bases for Quality Assurance of Chemical Measurements and Standards for Speciation", Dahlem Konferenzen, Proceedings of Workshop on the Importance of Chemical Speciation In Environmental Processes, Berlin, Federal Republic of Germany, 1984 (in press).
- Taylor, J. K., "Quality Assurance of a Measurement Program," (to be published in an ACS Monograph on Environmental Sampling)
- Taylor, J. K., "Validation of Analytical Data", (to be published in Marine Chemistry).

b. Talks

- Becker, D. A., "The NBS Recycled Oil Program: 1976 to 1983", at Fifth International Conference on Used Oil Recovery and Reuse, November 14, 1983, Las Vegas, Nevada.
- Becker, D. A., "Analysis for PCBs in Used and Lubricating Oils", Las Vegas, Nevada, November 16, 1983.
- Hertz, H. S., "Specimen Banking, Quality Assurance and Reference Materials (Their Interrelationships and Roles in Monitoring Programs)", National Bureau of Standards, Gaithersburg, MD, September 21, 1983.
- Hertz, H. S., "Role and Needs in Biological Reference Materials and Reference Method", Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 27, 1983.
- Hertz, H. S., "Interpretation of Mass Spectra", ADABSE Workshop, November 1983.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", ACS Short Course, Eastman Kodak Co, Rochester, New York, October 1983.
- Taylor, J. K., "Principles of Quality Assurance", Western Carolina Section, ACS, Clemson University, Clemson, SC, November 1983.
- Taylor, J. K., "Principles of Quality Assurance", Northeast Georgia Section, ACS, University of Georgia, Athens, GA, November 1983.
- Taylor, J. K., "Principles of Quality Assurance", Georgia Section, ACS, Agnes Scott College, Atlanta, GA, November 1983.
- Taylor, J. K., "Principles of Quality Assurance", Wilson Dam Section, ACS, Florence, AL, November 1983.
- Taylor, J. K., "Principles of Quality Assurance", Mississippi Section, ACS, Mississippi State University, Starkeville, MI, November 1983.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", ACS Short Course, Houston, TX, November 1983.
- Velapoldi, R. A., Organized Molecular Spectrometry Session and gave lecture "Ultraviolet-visible and Luminescence Spectroscopy", ADABSE Workshop, November 1983.
- Becker, D. A., "Quality Assurance Techniques for Activation Analysis", Fifth International Conference on Nuclear Methods in Environmental and Energy Research, April 4, 1984, Mayaguez, Puerto Rico.
- Hertz, H. S., "Ultratrace Organic Analysis", AFTACTND, Patrick Air Force Base, Florida, January 10, 1984.
- Hertz, H. S., "Clinical Chemistry at the National Bureau of Standards", Health Industry Manufacturers Association, Washington, DC, January 11, 1984.

- Hertz, H. S., "Chemical Measurements for Industrial Applications of Biotechnology", Eastman Kodak Company, Rochester, NY, June 29, 1984.
- Hertz, H. S., "Recent Applications of Isotope Dilution Mass Spectrometry", American Association for Clinical Chemistry, Washington, DC, August 3, 1984.
- Hertz, H. S., "Ten Years of Chemical Analysis: A Decade to Trace", Federation of Analytical Chemistry and Spectroscopy, Philadelphia, PA, September 17, 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", NBS sponsored Short Course, Clark County Sanitation District, Las Vegas, NV, January 1984.
- Taylor, J. K., "Quality Assurance of a Measurement Program", EPA Symposium on Environmental Sampling, Las Vegas, NV, February 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", ACS Short Course, Nalco Chemical Co., Chicago, IL, February 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", ACS Short Course, Pittsburg Conference, Atlantic City, New Jersey, March 1984.
- Taylor, J. K., "Statistics for Chemists", Pittsburgh Conference, Atlantic City, New Jersey, March 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", NBS sponsored Short Course, U. S. Geological Survey, Menlo Park, CA, March 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", ACS Short Course, St. Louis, MO, April 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", NBS-UNIDO sponsored training course, Shanghai Institute for Testing Technology, Shanghai, China, April, 1984.
- Taylor, J. K., "On Validation of Analytical Data", VIII International Conference on Chemistry of the Mediterranean Sea, Primosten, Yugoslavia, May 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", NBS Short Course, NBS, May 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", NBS Short Course, May 1984.
- Taylor, J. K., "The Use of Control Charts in Analytical Chemistry", Ruder Boskovic Institute, Zagreb, Yugoslavia, May 1984.
- Taylor, J. K., "Quality Assurance of Chemical Measurements", NBS sponsored Short Course, EPA-EMSL, Cincinnati, OH, June 1984.
- Taylor, J. K., "Data Quality - What QA is All About", Keynote Address, Johnson Conference of ASTM Committee D-22, Johnson, VT, July 1984.

Velapoldi, R. A., "The Center for Analytical Chemistry: Chemical Compositional Measurements of Materials", Department of Defense - JDL Technical Initiatives Panel on Advanced Materials, National Bureau of Standards, Gaithersburg, April 18, 1984.

Velapoldi, R. A., "Trends/Requirements in Analytical Chemistry", Doe - Health and Environmental Research (OHER) Workshop on Chemical Measurement Needs in Energy-Related Health and Environmental Research, Battelle-Seattle Conference Center, Seattle, WA, May 14 -16, 1984.

Velapoldi, R. A., "Microspectrofluorimetry: Standards and Measurements", University of Leiden, Leiden, The Netherlands, June 28 - 29, 1984.

Velapoldi, R. A., "Quality Assurance in Chemical Measurements", Dahlem Konferenzen, Workshop on The Importance of Chemical Speciation In Environmental Processes, Berlin, Federal Republic of Germany, September 1 - 8, 1984.

c. Committee Assignments

Harry S. Hertz

Secretary, American Society for Mass Spectrometry

Member, ASTM, Committee D19 on Water

Member, CEQ, Interagency Task Force on Environmental Data and Monitoring Air Pollution Data and Monitoring Working Group, Task Group in Anticipatory Monitoring

President-Elect, NCCLS

Technical Advisor, OIML, SP26, Subcommittee SR5 on Reference Materials for Calibration of Instruments Meant for Checking

Substances During Medico-Biological and Research Analyses

Member, Analytical Laboratory Managers' Association

Member, Department of Energy Health and Environmental

Research Advisory Committee

Rance A. Velapoldi

Member, Interagency Toxic Substances Data Committee

Working Advisor, ASTM, Committee E7 on Nondestructive Testing,

Subcommittee E7.03 on Liquid Penetrant and MPI Methods, Task Group E7.03.03 on E-270 Glossary Revision

Member, ASTM, Committee E13 on Molecular Spectroscopy, Subcommittee

E13.06 on Molecular Luminescence

Task Group E13.06.01 on Presentation of Corrected Fluorescence Spectra

Task Group E13.06.02 on Recommended Practices on Molecular Fluorescence Spectroscopy

John K. Taylor

Member, ISO/TC48, Glassware and Related Apparatus

ISO/TC48/SC01, Volumetric Glassware

ISO/TC146, Air Quality

ISO/TC01, Stationary Source Emission

ISO/TC02, Work Place Atmospheres

ISO/TC03, Ambient Atmospheres

ISO/TC04, General Aspects

Chairman, ASTM D19.01, International Standards  
ASTM D22, Sampling and Analysis of Atmospheres  
Member, ASTM D19, Water  
ASTM D19.02, 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 D22.09, 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 Museum Committee  
NBS Performance Review Board, SES  
NBS Representative - Interagency Advisory Committee on Water Data

Donald A. Becker

Member, ASTM, Committee D-2, Petroleum Products and Lubricants  
Subcommittees B, C, E, L, N, and PA. Publications

d. Other

a. Conferences

H. S. Hertz and R. A. Osteryoung, Chairmen, 37th Annual ACS Summer Symposium on Analytical Chemistry, "Trends and Accomplishments in Electroanalytical Chemistry," National Bureau of Standards, Gaithersburg, MD, June 11-14, 1984.

e. Center Colloquium Series

November 2, 1983 - Professor Raymond E. Dessy, Department of Chemistry, Virginia Polytechnical Institute, Blacksburg, VA, "The Rational Electronic Laboratory".

January 12, 1984 - Dr. Gunther Knapp, Institute for Analytical, Micro- and Radiochemistry, Technical University of Graz, Graz, Austria, "Some New Techniques for the Decomposition of Organic Materials in Trace Element Analyses".



- January 18, 1984 - Dr. M. James Blackman, Conservation Analytical Laboratory, Museum Support Center, Smithsonian Institution, Washington, D.C., "Smithsonian Institution- NBS Cooperative Programs".
- February 8, 1984 - Professor Stanley N. Deming, Chemistry Department, University of Houston, Houston, TX, "Optimization in Chemistry".
- March 14, 1984 - Dr. Norman Anderson, Argonne National Laboratory, Argonne, IL, "The Human Protein Index: Scope, Technology, Standardization and Data Base".
- August 27, 1984 - Professor Nicolo Omenetto, CCR, European Community Center (Euratom Joint Research Center), Stabilimento di Ispra, "Analytical Laser Spectroscopy at the Joint Research Center of Ispra, Italy".

## B. Voluntary Standardization and Quality Assurance

### 1. Voluntary Standardization

The Center continues to play an important role in standardization activities. Thirty-five members of the staff hold 137 memberships on standards committees, including positions of leaderships on 9 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-07	Nondestructive Testing
ISO/TC146	Air Quality
ISO/TC147	Water Quality
IUPAC	Commission on Atomic Weights
NCCLS	National Committee for Clinical Laboratory Standards

ASTM Awards of Merit were presented to John A. Norris (551) and to John K. Taylor (550) in recognition of their contributions to the advancement of voluntary standardization.

### 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.

Seminars of the first type were presented three times at NBS during the past year to a total of 140 persons, largely from various industrial organizations. Three of the second type were presented to other government agencies with a total attendance of 95 persons. The latter has also been presented six times as an ACS short course to a total of 196 persons. This swells the total to 1627 persons who have attended one of these seminars since the series was started.

The seminar was presented at the Shanghai Institute for Testing Technology (SITT), Peoples Republic of China, during a 3 week period in April 1984, under UNIDO sponsorship. Eighteen half-day sessions were needed to cover the material, consisting of sequential translation from English to Chinese. Some 57 persons from 22 different technical institutes in the Shanghai area attended. In addition, a half-day overview of modern quality assurance was presented to 158 members of the Shanghai Association for Science and Technology. The lectures in the series were taped and are being translated for publication in the Chinese language, by SITT. In addition to the above, a general lecture on quality assurance has been presented five times during the past year to a total of 425 persons.

Two additional routes for extending the quality assurance influence of the Center have been undertaken during the past year. One of these consists in the preparation of a "Handbook for SRM Users" which discusses the philosophy of quality control of the measurement process and of the use of SRM's for quality assessment of the measurements. Both general and practical information is presented in the handbook which will be published within the year as an NBS 260 series publication.

A generic quality assurance guidance document, "Principles of Quality Assurance," has been prepared, under NOAA sponsorship, for use in the National Marine Pollution Program (NMPP). The document will be initially distributed at a NOAA-sponsored workshop to be held at NBS in December 1984, in which the several government agencies involved in the NMPP will participate. Although prepared for the NMPP, the document, due to its generic nature, should be useful to most laboratories developing a quality assurance program for specific measurement problems.

Closely related to the above, a "Quality Assurance Handbook for State Weights and Measures Laboratories," has been prepared under sponsorship of the NBS Office of Weights and Measures. This handbook contains 15 standard operating procedures for the calibrations made most frequently by these laboratories together with a collection of good laboratory practices and good measurement practices related to them. Additional information contained includes statistical techniques for data evaluation and discussions of control charts. The handbook is expected to be ready for distribution by the end of 1984.

John K. Taylor

C. Service Analyses

Service analyses are 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 standards 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 recalibration of SRM gas mixtures and for the verification of spectrophotometric transmittance SRM's.

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 inter-division work order and designated cost centers are cross-charged. All outside work is performed on a purchase order.

During the first 11 months of FY84, CAC staff provided analyses or recalibrations for some 98 requests at a cost of \$273,800. These requests and their associated funding were divided among the three categories of customers as follows: NBS - 17 jobs (\$36,700); other government agencies - 26 jobs (\$150,900); and private industry - 55 jobs (\$86,200).

R. W. Burke

## 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 five groups which are oriented to specific technical disciplines. The groups are: Activation Analysis, Analytical Mass Spectrometry, Atomic and Molecular Spectrometry, Electroanalytical Chemistry, and Laser Analytical Chemistry which was transferred from the Center Office during this past year.

The Division strives to maintain a satisfactory balance between research and development of analytical methods and analysis of materials such as SRM's that serve as critical analytical tiepoints to accuracy. At present, considerable effort on research is needed to provide the capability necessary to keep up with the latest developments in high accuracy analytical measurements. Too often in the past our need to concentrate on problems with the analysis of specific materials has diverted attention from maintaining our state-of-the-art capability. Nevertheless, we have made significant progress in our research program.

The study of laser photoionization processes has resulted in significantly improved ionization efficiencies for a number of elements. As a result, a new series of elements may be determined by isotope dilution mass spectrometry. The neutron depth profiling (NDP) technique continues to increase capability, particularly with respect to depth resolution which is of crucial importance to the solid state electronics industry. This project is drawing the attention of a number of materials scientists both from industry and universities (Technical Report 2, page 24). Many of the current manufacturers of solid state (silicon) devices are working with us to evaluate the technique. Another major accomplishment is that relative standard deviations approaching 0.5% have been attained with precise gamma-ray counting. This opens up major new opportunities for activation analysis including the determination of macroconstituents in SRM's and the measurement of isotope ratios which has application in a variety of tracer studies as well as the Division's atomic weight program.

The need for the accurate measurement of acidity, as related to the measurement of acid rain, generates controversy regarding the convention of using pH as the indicator. Since the term relates to the thermodynamic activity and not hydrogen ion concentration, the necessity for evaluating ionic strength and liquid junction potential when electrochemical measurements are made, requires that standards be used that approximate (rather closely) the "real" samples that are to be measured. The leaching properties of acid rain probably relate to hydrogen ion activity rather than concentration; therefore, studies to eliminate the systematic errors due to sample

type are very important. Using diluted strong acids as standards will help with part of the problem and some recent ideas on the reduction of the liquid junction potential must be pursued (see Technical Report 19, page 38).

Often neglected research components of the analytical process are chemical dissolution, blank reduction, and chemical separation. There are a number of advances in technology which allow energy to be selectively added to the sample so as to minimize losses of sample constituents during the dissolution step and thereby improve the accuracy of the analysis. In addition, the recent trend is to do as little chemical separation of the elements as possible, and to rely on the instrumental methods for eliminating interferences. While in some cases such reliance appears to be well founded, in others, the appearance of errors due to interference resulting from incomplete instrumental selectivity is well documented. While chemical separation procedures are labor intensive, it is important that we continue to study this area, and although we analyze a variety of sample types throughout the year which makes automation difficult, it may still be possible to automate some of the separation and dissolution steps.

Particularly noteworthy is the work of three of our staff members who received IR-100 Awards from the publication, Industrial Research. (See Technical Report 18, page 37 discussing the use of the vibrating electrode in voltammetry and Technical Report 20, page 39 discussing the use of sulfur isotopic tracers in the environment.) These are the first such awards in the Division and we are very proud of these accomplishments.

A large number of samples have been analyzed this year as part of our extensive contribution to the SRM program (Technical Report 21, page 40) along with the service analyses which we routinely perform. The distribution of effort in the certification process among the groups in the division is somewhat non-uniform. A program is in place to correct this situation. In addition, a great deal of effort has been invested in analyzing samples from Other Agencies. Many of these samples relate to the "calibration" of agency-made standards to be used as quality assurance materials for their own laboratories. In the future, we will continue attempts to assist such agencies in the formulation, design, and generation of these materials so as to improve the overall utility of their quality assurance programs and provide materials with traceability to CAC.

During this past year, the Division has substantially increased its interactions with other scientists in industry, other government agencies and universities both in this country and abroad. This has resulted in a significant number of guest workers who have joined the various groups in the Division for periods of time ranging from a few months to two years. The sharing of ideas has proven beneficial to both of us.

Future plans involve combining an in-depth understanding of the systematic and random errors present in the analytical methods routinely used in the Division with as much automation, robotics, and computer control as possible without compromising the analytical accuracy. This would lead to a significant increase in the effectiveness of the Standard Reference Material program. In addition to improving the accuracy of the certification-measurements, throughput will be increased, and a wider variety of sample types will be certified.

## 1. Activation Analysis Group: Overview

The development and application of nuclear analytical techniques for greater accuracy, higher sensitivity and better selectivity are the goals of the Activation Analysis 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), and in LINAC-based activation analysis using photons (PAA). In addition, the group has a unique capability in neutron beam analysis with both prompt gamma activation analysis (PGAA) and neutron depth profiling (NDP). The NDP technique utilizes prompt charged particle emission to determine elemental distributions within the first few micrometers of a surface while the PGAA technique utilizes prompt gamma-ray emission to measure the total amount of an element regardless of its location in the sample. These techniques provide an arsenal of tools to address a wide variety of analytical problems in science and technology.

During the past year, research efforts in INAA have been directed toward extending its multielement capability by investigating short-lived activation products ( $T_{1/2} = 1$  s) and epi-thermal activation analysis using shielded irradiations. The work with RNAA has continued to expand the number of elements which can be quantified at or near the theoretical detection limit of the method. Especially challenging have been gas-phase radiochemical separations which have allowed routine measurement of  $^{129}\text{I}$  at the  $10^8$  atoms per gram level. Work on the certification of U-235 standards has demonstrated that a precision well below 0.1% can be achieved with gamma-ray spectrometry. Since random counting uncertainty is the ultimate limitation on the accuracy of all activation measurements, the challenge now exists to understand and, where possible, reduce systematic errors to below the 0.1% level.

During the past year, there has been a continuing effort in the area of trace element analysis of biological materials. In addition to the ongoing work on biological Standard Reference Materials and the Pilot Environmental Speciman Book program, several new research areas have been established. Activation analysis is being used to study the interrelationships among trace elements, bioanalytical separations, and biological macromolecules. Of particular interest is a beginning effort employing a chromium isotope dilution technique to measure the increase in total blood volume during pregnancy.

With the success of the Bureau's initial effort to establish a National Facility for Cold Neutron Research at the NBS Reactor (NBSR), both of the Group's neutron beam techniques, PGAA and NDP, have the potential of improving in sensitivity and throughput by at least a factor of one hundred. The increased neutron intensity and reduced background will allow, for example depth profiling of nitrogen and chlorine by NDP and the prompt gamma determination of hydrogen and boron at the ng/g levels. This will give the Bureau an unprecedented ability for chemical compositional analysis of materials such as metals, glasses, and semiconductors as well as more complex matrices.

The coming year will see an upgrade of the NBSR from its present 10 MW power level to the full design power of 20 MW. This will provide a factor of two improvement in many of our activation analysis sensitivities and in all of our PGAA and NDP analyses. While this upgrade is taking place, we will

install a new data acquisition system based on a VAX computer to replace the outgrown 16-bit system now in use. In addition to the control and processing of gamma ray spectra now carried out, the enhanced computational capability will be used for substantially improving the modeling of the activation analysis process to improve its accuracy.

Ronald F. Fleming, Group Leader; M. James Blackman, B. Stephen Carpenter, R. Greg Downing, Kathleen A. Fitzpatrick, Robert R. Greenberg, G. Yenkaresh Iyengar, John K. Langland, Richard M. Lindstrom, George J. Lutz, John T. Maki, Susan F. Stone, Rolf L. Zeisler

## 2. Analytical Mass Spectrometry Group: Overview

The Analytical Mass Spectrometry Group develops and maintains the capabilities required to perform compositional measurements using the analytical sciences of chemical separation and mass spectrometry. For many years, the Group has been involved in chemical separations, plus the highly precise and accurate isotope ratio measurements required to determine the atomic weights of the elements and to make very definite measurements of trace element concentrations. While maintaining the basic thrust in the traditional areas, the horizons of the Group have broadened markedly in the past few years. Predicated on the competence building program and related basic research, substantial changes have been initiated to develop new capabilities for chemical separations and ion spectroscopy. By combining the foundation evolved from many years of measurement research and applications with the recently initiated fundamental changes described below, we anticipate that a new generation of measurement capabilities for analytical mass spectrometry and compositional analysis will be achieved.

Research in the ion mechanisms competence building program has resulted in several significant accomplishments during the past year: resonance ionization mass spectrometry (RIMS) has been used to extend the demonstration of ionization feasibility to twenty-eight elements; a systems calibration using  $^{57}\text{Fe}/^{56}\text{Fe}$  ratios has been completed for the RIMS system; the RIMS system has also been used for isotope dilution analysis of iron in SRM's; auto-ionization levels and the spectroscopy of previously unobserved Rydberg structures have been studied for beryllium in collaboration with personnel from the Center for Radiation Research; the systematics have been explored for multielement analysis, and seven elements in a mixture have been selectively ionized. Research has also been initiated to study thermal molecular positive ion formation that will lead to the determination of isotope ratios and elemental concentrations by isotope dilution for elements such as Se and Te.

Several of the Group's technical outputs have been highlighted in the following Technical Reports. Not included are a number of other areas that contribute substantially to the overall output and technical support. The RIMS laboratory has been expanded and equipment installed to initiate an all-new narrow bandwidth, high sensitivity RIMS system; isotope dilution procedures have been developed to determine ultra-trace levels of vanadium in biological materials; the gaussmeter-controller on the mass spectrometers have been modified to permit digital control; and the first prototype of a new electrometer has been completed to replace commercially unavailable components. The NBS-Smithsonian collaboration has continued for the use of lead isotope ratios in the provenance determination of archaeological



artifacts, with much of the activity focusing on Chinese artifacts. In addition to these activities and projects, members of the Group have carried a substantial load of SRM certification work, and have provided quality services for Other Agencies, ranging from consultation, to high precision isotope ratio measurement, to designing and building instrumentation and electronics.

A substantial contract has been negotiated with a major chemical manufacturer to utilize the Division's unique trace element measurement capabilities to examine the purity of fluorocarbon polymers. This project reflects a synergistic interest in the reduction of impurities in state-of-the-art containers, reagents and materials.

Plans for next year include investigations of the analytical capabilities of inductively coupled plasma mass spectrometry, (ICP-MS). The ICP-MS system also will be evaluated for its applicability to isotope dilution analysis, and mechanisms of material transport to the spectrometer will be investigated. A collaborative effort with the Surface Science Division, Center for Chemical Physics has been initiated to examine the sample transport and energy transfer mechanisms associated with the ion bombardment sputtering of solids. For this purpose, time-of-flight RIMS will be used as an energy state-specific probe to examine the nature of the sputtered neutral and ionic species, and to evaluate the resonance ionization pathways required for the studies. Initial progress on the investigation of molecular ions formed by thermal processes will continue in an attempt to understand the ion formation process and to provide a basis for ultra-trace determinations of selenium and tellurium by isotope dilution mass spectrometry. Research efforts will also be initiated for the determination of the atomic weights of lithium and nickel. As part of this effort, the importance of fringing field effects will be assessed for lithium isotopic measurements. Substantial progress is also anticipated in the ensuing year for the automation of chemical separation procedures, and for the development of microwave dissolution technology. Research in these two areas - dissolution and separations - has progressed smoothly during the last year, and significant milestones should be achieved during the next year. At the interface between the competence building program and an other agency project, we will further develop RIMS technology directed toward the measurement of small numbers of  $^{129}\text{I}$  and uranium atoms. Finally, we will continue to explore the potential of stable isotope tracers in the environment. Through these efforts, and by the maintenance of quality services to the OSRM and other agencies, we hope to achieve a balanced program of growth in newer technical areas, while maintaining a solid and progressive foundation in the traditional areas of high accuracy isotope dilution mass spectrometry.

We are most pleased to announce that Paul Paulsen and Bob Kelly have been awarded one of the coveted and competitive IR-100 awards for their research on sulfur isotopic measurements (see Technical Report 20, page 39). Dr. Heinz Zeininger from the laboratory of Prof. Klaus Heumann has joined our group for a one year stay as a foreign guest worker from the University of Regensburg, Regensburg, Germany. Dr. Zeininger will interact principally in the research areas of RIMS and negative thermal ionization mass spectrometry.

L. J. Moore, Group Leader; I. L. Barnes, E. S. Beary, W. A. Bowman, III, K. A. Brletic, E. C. Deal, J. D. Fassett, J. W. Gramlich, S. A. Hotes, L. B. Jassie, W. R. Kelly, H. M. Kingston, G. M. Lambert, L. A. Machlan,

J. R. Moody, T. J. Murphy, P. J. Paulsen, L. J. Powell, D. W. Schwartzman, R. W. Shideler, R. J. Zeininger.

### 3. Atomic and Molecular Spectrometry Group: Overview

The principal objectives of the Atomic and Molecular Spectrometry Group are to conduct research in the fundamental processes in spectrochemical analysis and to apply the results of this research to compositional measurement problems and the characterization of Standard Reference Materials. This research involves the study of basic processes in chemistry and physics and is directed toward improving the precision and accuracy of the methodology.

During the past year, the major activity of the Group has been in characterizing Standard Reference Materials (SRM's), participating in programs of national concern, providing service analyses on highly complex samples for other government agencies and industry as well as other divisions at NBS, and providing a training program for guest scientists. To accomplish these activities, the following techniques were used extensively: atomic absorption spectrometry (AAS); optical emission spectrometry (spark); inductively coupled plasma emission spectrometry (ICPES); direct current plasma emission spectrometry (DCPES); gases in metals; and uv-vis spectrophotometry.

Research on the mechanism of material transport is continuing. Results from this study should play an important role in explaining the fundamental processes in the spark discharge which affects the transport of bulk sample to a measurable state. In addition, the feasibility of coupling the spark discharge with other excitation sources such as an air-acetylene flame or a direct current plasma is under investigation. A cooperative effort with the Laser Analytical Chemistry Group was initiated this year to couple various analytical spectroscopic techniques with laser probes. Laser fluorescence in flames and laser enhanced ionization in the ICP were studied to evaluate sensitivity and interferences encountered in these techniques for trace elemental analysis.

The Group is participating in a project for the development of luminescent glass spheres to serve as standards for calibrating microspectrofluorimeters used in quantitative immunofluorescence assay. Glass compositions which produce both broad and narrow band emission spectra are being evaluated.

The work in the area of gases in metals has continued. Methods developed for the determination of carbon, sulfur and hydrogen have been utilized to certify a number of new SRM's with improved precision and accuracy. These techniques are now used also to carry-out the numerous homogeneity studies routinely required in the metals program and for a variety of service analyses.

Optical emission spectrometry (spark) was used extensively in homogeneity studies of SRM's (aluminum alloys, irons, steels, brass-bronzes and leads). The planning and monitoring of the production of an SRM Battery Lead

and a replacement low alloy steel are underway. An interesting project involved the determination of chemical composition of flanges for photomultiplier tubes on a current satellite project for NASA. Of the several alloys tested, NASA determined that only one alloy was suitable as a flange material.

A major part of the overall group effort involved the characterization of 22 different SRM's for 75 major, minor, and/or trace elements by AAS, DCP, ICP and spectrophotometry. The materials characterized varied considerably and included brick clay, coal, rutile, oil, urine, and botanicals. To determine 11 elements in the brick clay, three different dissolution procedures (two basic fusion and a wet oxidation method) were developed to prepare this refractory material for the final DCP and AAS measurements. AAS and ICP were used to determine 22 elements in the SRM Coal which required four separate dissolution procedures to prepare the material for final analysis. A comparison between Zeeman and deuterium arc methods for background correction of AAS was made during the characterization of lead in whole blood. The blood-lead method previously developed at NBS was used to demonstrate that the two methods were in good agreement. AAS with electrothermal atomization was used to determine trace elements in human liver, acid rain, and germanium which is being clinically evaluated as an anti-neoplastic agent on carcinoma cells and as an anti-malaria drug at Georgetown University Hospital. Samples of serum, plasma, red blood cells, urine, and bile from patients treated with the drug showed a marked decrease in germanium concentration with time. Additional tests are planned to determine the fate of the germanium.

An additional capability now exists for determining fluoride in urine and similar liquids in which the fluoride is present in ionic form. The new procedure entails separation of fluoride from the sample matrix as HF, collection by absorption in an alkaline solution, and determination of the separated fluoride by spectrophotometry. A study of different organic solvents to improve the analytical accuracy of trace elemental analysis by ICP was undertaken; however, no single solvent was found to be the best for all elements. Consideration of signal-to-background ratios as well as background structure near the analyte peak wavelength were found to be critical in choosing the best solvent for a particular element.

Another significant investigation was the evaluation of AAS with hydride generation and chelation-solvent extraction techniques for the separation, preconcentration, and determination of total tin and tributyltin from seawater. Tributyltin oxide is extremely toxic and is used as an antifouling coating for ships' hulls. The toxic compound leaches from the coating matrix which discourages settling forms of marine organisms. Plans are underway to continue this study and to expand it to the analysis of sea sediments and soft tissue.

In high accuracy spectrophotometry, significant progress has been made in the production of SRM Glass Transmittance, Metal-on-Quartz, and Stray Light Attenuation Filters. The wedge effect, reported last year, has not been completely resolved, but work is continuing in this area. Our initial

work to extend the measuring capability of the NBS-CAC high accuracy spectrophotometer into the near-infrared region of 0.8 to 2.4  $\mu\text{m}$  was not accomplished because of the inability of the vendor to deliver optical components. As a result, a design for this extension into the near-infrared has been developed in house, and the system is under construction.

Research during the coming year will focus on several areas. In material transport studies, techniques used to characterize the physical properties and chemical composition of pure elements and brass alloys will be extended to more complex materials. Also, the use of mobility particle counts as an indicator of the amount of material sampled by the spark will be investigated. Studies of flow injection sample introduction and ultrasonic sample nebulization for DCPES and ICPEs will continue. Accurate, discrete microsample introduction is facilitated by the use of a rapid wavelength-modulation background correction device in the echelle spectrometer of DCPES. The continuous flow mode of the flow injection system permits automated standard addition and sample buffering. The technique of ultrasonic sample introduction has the potential of increasing the analytical sensitivity of many analytes in ICPEs and DCPES. The problem of sample memory encountered with ultrasonic nebulization has been corrected with a new cell design. Plans are underway to re-establish some of the classical techniques for gases-in-metal to check the accuracy of our present gases-in-metals instrumentation. Methods to be utilized include the Kjeldahl method for nitrogen, the classical gravimetric and potentiometric methods for hydrogen and oxygen, and a 14 MeV nuclear activation technique for oxygen. Also, a study of various ways to introduce samples into the inductively coupled plasma-mass spectrometer should provide improvement of the sensitivity of this technique and suppression of matrix interferences.

Theodore C. Rains, Group Leader; David E. Brown, Robert W. Burke, Therese A. Butler, Barry I. Diamondstone, Michael S. Epstein, Radu Mavrodineanu, De-ming Mo, John A. Norris, Theresa A. Rush, Joichi Ueda, Robert L. Watters, Jr., Yong-Kang Zhang.

#### 4. Electroanalytical Chemistry Group: Overview

The Electroanalytical Chemistry Group conducts basic research and utilizes electrochemical principles to develop techniques and 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 processes encountered in the development and implementation of electroanalytical methods.

A major effort in the past year has involved the measurement of pH in various matrices, for example in low ionic strength solutions, which is of great utility for acid rain programs. It had been previously established in our laboratory that the residual liquid junction potential was the dominant source of error in such measurements. Research was conducted to develop improved measurement procedures and to develop new pH calibration standards which would minimize this error. The results of a round-robin exercise indicate that matrix specific pH standards significantly improve the precision and accuracy of the measurement if a definite procedure is followed explicitly. A ruggedness test of the procedure is now underway to determine the degree of control necessary for each component of the procedure. A new

Research Material, RM 8409 Simulated Rainwater, has been developed to aid in the analysis of rainwater. Work will continue on this project to develop a Standard Reference Material for rainwater. (See Technical Report 19, page 38).

Efforts in other aspects of pH measurement research continue with the certification of a new lot of potassium acid phthalate for pH, SRM 185f (one of the most widely used pH buffer materials) and the certification of two materials for pD, potassium acid phthalate and sodium bicarbonate/sodium carbonate. A more reliable procedure for preparing stable and reproducible silver/silver chloride reference electrodes has been developed and fundamental studies of the standard potential of this electrochemical couple are in progress. A collaborative effort in this endeavor has been initiated with the Radiometer Corporation. Thermodynamic studies in deuterium oxide have also been conducted. The use of a silver chloride membrane as an ionic conductor instead of the conventional liquid junction barriers has been preliminarily tested. This effort will require considerable research, but appears very promising.

Research in voltammetry has included the development of a flow-injection system using a vibrating wire electrode detector. The main advantages of this system are improved sensitivity due to increased mass transport to the electrode and the ability to investigate hydrodynamic modulation independent of sample flow-rate. Dr. Pratt received an IR-100 Award for this achievement. Diffusion processes at ultramicro wire electrodes have been studied, and the effects of surface roughening explored. A new method for the determination of Cr(VI) has been developed using vibrating wire electrodes both in a conventional cell and in the flow-injection mode. The electrode can be either gold or palladium. The method is free from interference of chromium in other valence states, iron and chloride. (See Technical Report 18, page 37).

Advanced ion chromatography instrumentation has been acquired and will be used to improve the determination of anions via better sensitivity and selectivity. It will also be used to extend our capabilities to the determination of the alkali metals and ammonium, and ultimately, to the alkaline earth and transition metals. The existing instrument has been used extensively this year in the analysis of SRM coals and oils, of rainwater audit and research materials, and in research to develop a new method for the determination of fluoride in biological materials.

Coulometry in the controlled current mode has been used for high accuracy assays of the acidity of rainwater research materials, of the acidity of HCl and DCl solutions used in pH and pD research, and for the standardization of chloride solutions to be used as standards for activation analysis. Rutile Ore (SRM 670) was analyzed for titanium content by controlled potential coulometry.

Research has been initiated to develop advanced expertise in aqueous conductance measurements with the view towards issuing a SRM and towards understanding the fundamental relationships among conductivity, ionic mobility, diffusion, and ionic strength.

We continue to expand our resources and scope of research through active use of the postdoctoral and guest worker programs and industrial and academic collaborations. This year the group is composed of three permanent research chemists, one postdoctoral research associate, a visiting university faculty member, a guest worker from the People's Republic of China, and a summer student. In addition, Eva Deak from the National Office of Measures of Hungary will be visiting for one month to exchange information on pH measurement and research. The group maintains its involvement with ASTM and NCCLS through active participation in meetings and task groups. Efforts are still underway to identify a research associate to develop methods and reference materials for the potentiometric measurement of calcium in biological fluids.

Research in pH will continue as a long-term commitment to provide reliable and thermodynamically significant measurements and standards in this most widely used analytical parameter. 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, focusing on improved resolution and sensitivity. Flow-injection analysis with electrochemical detection will be implemented for determinations of trace metals in complex matrices. Voltammetry will be re-established as a valuable analytical research technique within the group. Determination of metal species by valence and by complexation will be a dominant research direction.

William F. Koch, Group Leader, Han Kai, Melissa Knoerdel, George Marinenko, Kenneth W. Pratt, Jr., Rubye P. Torrey (visiting faculty), and Yung Chi Wu

## 5. Laser Analytical Chemistry Group - Overview

The objective of this group is to develop new concepts for performing spectroscopic analysis. The major emphasis is in the use of lasers as spectroscopic probes and is centered about laser enhanced ionization (LEI), resonance ionization mass spectrometry (RIMS), and laser infrared diode spectroscopy. No major shift in direction is anticipated as a result of the group being transferred to the Inorganic Analytical Research Division.

A major review on the theory and development of the laser enhanced ionization in flames (LEIF) was completed this year. This paper was reviewed by Ph. Alkemade, a reknowned expert on the physics of analytical flames who stimulated our interest in extending our studies of the ion formation processes. In addition, calculations have been done on the time dependent electric field, ion, and electron densities that now enable us to prepare a major paper on the theory of the ion collection process. Our attention is now turned toward the theory of ion formation by photoexcitation processes both in LEIF and RIMS.

The analytical applications of LEIF are proceeding well. A major contribution was the work for Shell Development Laboratory and Sohio Research. (See Technical Report 7, page 28.) We also contributed to the measurement of some standards to be used for the calibration of inductively coupled plasmas for the EPA. The redesign of the apparatus has been delayed by the unavailability of software which will be used to incorporate the wavelength calibrator. However, progress has been made on automating the remainder of the system. We expect to continue analyzing samples for OSRM

and Other Agencies. In addition, we have received support from the Office of Standard Reference Materials to evaluate random and systematic errors in the technique.

A longstanding interest of this group is the generation of a new component of the atomic spectroscopic analytical system that can be identified as the sample transport-atom reservoir. If it can be ascertained that some type of device such as a spark or laser can transform material from the sample into a vaporous state without compositional bias, then use of an atom reservoir to contain the sample may result in an analytical system of very high accuracy with few, if any, matrix effects. Initial efforts are involved in a collaborative study with the Atomic and Molecular Spectrometry Group to determine whether material maintains integrity during the vapor-condensation process when transported. Results to date for the spark indicate a possible bias for a brass sample (see Technical Report 7, page 28 for more detail). We will develop more efficient procedures for collecting the aerosol that is produced and also we will investigate the potential of laser ablation for aerosol production.

Well over half of the effort of this group involves collaboration with other scientists in the Division, Center, and Bureau (several of these are described in other Technical Reports). In the Division -- Mass Spectrometry Group on RIMS and on Automation of Group Separations of the Elements; Atomic and Molecular Spectrometry Group on Spark Material Transport and Aerosol Characterization; Organic Analytical Research Division -- Mass Spectrometry Group on Laser Photofragmentation; and the Gas and Particulate Science Division -- Microanalysis Research Group on Material Transport Particle Analysis, Gas Metrology Group on the Analysis of Nitrous Oxide with the Ir Diode Laser and the design of a thermostated gas cell for freon analysis; the Atmospheric Chemistry Research Group on the HO<sub>2</sub> Radical and HCl; and the Center for Radiation Research, Instrumentation Group on the Design of a Spark Generator. We also have a major effort in laboratory automation both for the Group and others. A member of our Group chairs the NBS microprocessor storeroom committee and provides a significant service to the NML staff on matters pertaining to the NBS storeroom microprocessor system.

James R. DeVoe, Group Leader, Fillmer C. Ruegg, Robert L. Sams, John C. Travis, and Gregory C. Turk

B. Selected Technical Reports  
(Inorganic Analytical Research Division)

1. Determination of Boron in Borosilicate Glasses by Neutron Capture  
Gamma-Ray Activation Analysis (15310)

R. M. Lindstrom and J. E. Riley, Jr. (AT&T Bell Laboratories)

Optical waveguides are rapidly assuming a major place as media in data and voice communication. As part of a study of micrometer-scale spatial gradients in the composition of waveguide glasses, neutron capture prompt gamma-ray activation analysis has been used to determine the boron contents of seven borosilicate glass materials, ranging from 1% to 8% boron. This instrumental method does not require the dissolution of sample, which may be difficult to achieve for these materials.

A series of glasses was obtained from Corning Glass Works. The supplier provided information about nominal batch compositions, to within 20%, which was used to select the experimental parameters. Neutron self shielding can lead to substantial bias in these high-boron materials. The effect was minimized by diluting the powdered samples with high-purity graphite and by performing comparative analyses with SRM 93a Glass, diluted in a similar manner, as a standard in addition to the primary standard prepared from SRM 951 Boric Acid.

Measurements of the graphite and of pure quartz processed in the same way as the samples showed a blank of less than 150 ng B/g. When duplicate mixtures of glass and graphite and replicate portions of the same mixture were analyzed, the results showed that the samples were prepared with better than 1% reproducibility and homogeneity. Comparative analyses of the same materials by ICP-OES gave excellent agreement, the mean ratio between the two techniques being 1.00, with a relative standard deviation of 2.5%.

2. Neutron Depth Profiling: Development and Intertechnique Comparisons  
(15310)

R. G. Downing, J. T. Maki, and R. F. Fleming

During the past year, the technique of neutron depth profiling (NDP) has been significantly advanced through research and development, and industrial interactions. This is evidenced by the seven manuscripts that have either appeared or are in preparation for journal publication, most resulting from interactions with outside users of the facility. At present, these interactions include two research associates, four guest workers and more than ten other scientific collaborators from U.S. industries and universities.

Intertechnique studies formed a major thrust of this year's efforts. NDP was used as a reference technique between secondary ion mass spectrometry (SIMS) and spreading resistance profiling (SRP) for studies of boron implanted silicon wafers. Of particular importance was the ability of NDP to give reliable measurements of dopant profiles across interfacial boundaries of insulating and semiconductor materials. NDP is one of the few techniques that can be used to quantify accurately boron concentrations and profiles in insulating materials. In addition, NDP was used to referee an abundance discrepancy between the Auger electron spectrometry value for the implanted



nitrogen concentration in a tooling die metal and the surface dose recorded from the ion beam current of the implanter. This was the first time nitrogen profiles have been measured by NDP in a U. S. facility.

Three salient improvements have been made over the last year: (1) The background arising in the spectrum from neutron and gamma beam interactions with the target chamber has been reduced by a factor of three through the customizing of shielding components. This innovation has already been transferred to a collaborating NDP facility at the University of Michigan. (2) Interactive computer software was developed to model implant profiles, allowing NDP spectra to be deconvolved. The software has been particularly useful in unfolding helium and nitrogen profiles in semiconductor and metal samples. (3) It was demonstrated that by measurement of concentration profiles at low grazing angles with respect to the sample surface the depth resolution of NDP could be improved by more than a factor of three. Through comparison with SIMS and this type of shallow angle NDP profiling, artifacts arising at SiO<sub>2</sub>/Si interfaces in SIMS spectra are being studied and methods are being developed to correct the SIMS profiles.

Future directions include developing NDP into a multidimensional technique through the use of position sensitive detector systems and greater efforts in spectral deconvolution. Of the many applications for two-dimensional NDP, nondestructive lateral diffusion studies of dopants and their concentration on the submicrometer scale offer immediate benefit to semiconductor research. Also, investigations of grain boundary segregation of mobile constituents in high-technology alloys would be of widespread utility. Through these developments, NDP is becoming increasingly useful and applicable as a research and development tool for industry and science.

### 3. High Accuracy Determination of <sup>235</sup>U in Nondestructive Assay Standards by Gamma-Ray Spectrometry (15310)

B. S. Carpenter and R. R. Greenberg

High precision gamma-ray spectrometry measurements have been made on five sets of uranium isotope abundance Standard Reference Materials (SRM's) for nondestructive assay (NDA). These sets, SRM 969, were prepared in a joint effort with the Commission of European Communities' Central Bureau of Nuclear Measurements (CBNM) and are intended for international safeguards use as primary reference materials for the determination of the <sup>235</sup>U abundance in homogeneous uranium material by gamma-ray spectrometry. The measurements consisted of determining the counting rate uniformity of the <sup>235</sup>U 185.7 keV gamma rays as well as the <sup>235</sup>U isotope abundance for each sample. Since the samples were packaged so the U<sub>3</sub>O<sub>8</sub> was infinitely thick for the 185.7 keV gamma ray, the measured counting rate was nearly independent of the material density. In addition, the activity observed by the detector was collimated to simulate calibration conditions used to measure bulk material in the field.

The isotope abundances for all five sets, as determined by gamma-ray spectrometry, agreed with the average of the thermal ionization mass spectrometry values to  $\leq 0.1\%$ . The measurement variations within the 5 sets of samples ranged between 0.05 - 0.11% (1s) with standard deviations of the mean ranging from 0.01 - 0.02%. This observed variation appears to be due predominantly to counting statistics and not to material inhomogeneity and/or packaging.

The results of this study indicate that accuracy of  $^{235}\text{U}$  determination via gamma-ray spectrometry, in the range of few hundredths of a percent (2 sigma), is achievable. The main requirement for achieving this level of accuracy is a set of counting standards whose  $^{235}\text{U}$  isotope abundances are known to within 0.01% (2 sigma).

#### 4. Accurate Multi-Element Analysis of an Aquatic Accumulator (15310)

S. F. Stone, R. Zeisler and R. Sanders (Pacific Northwest Laboratories)

A joint research program, involving the National Bureau of Standards and the Environmental Protection Agency, has been concerned with the study of biological specimens as monitors of the marine environment. Several analytical techniques were used to obtain concentrations for over 40 elements in selected specimens. Steps were taken to assure the accuracy of the reported measurements by avoiding contamination not only in the chemical analyses, but also during sampling and sample preparation. This was especially important for elements occurring at trace levels.

The organism selected as the monitor for the marine environment was Mytilus edulis, a marine mussel. The mussels were collected under controlled conditions, separated into batches, and stored. Before analysis, the mussels were shucked and then cryogenically homogenized. Three instrumental techniques were then applied sequentially for analysis; (1) backscatter with fundamental parameter X-ray fluorescence (BFP-XRF), (2) neutron-capture, prompt-gamma activation analysis (PGAA), and (3) instrumental neutron activation analysis (INAA). The same 300 mg portion of mussel homogenate was analyzed in sequence by each instrumental technique.

Several checks were instituted during the study to evaluate the accuracy of the concentrations obtained. These included intercomparison of the three different techniques and the analysis of Standard Reference Materials to evaluate the data following analysis. Using the same 300 mg portions for the sequential analyses eliminated questions of problems in agreement due to inhomogeneous material. Possible contamination from the homogenization, sampling, and storage processes was investigated with an ultrapure water blank, and found to be negligible.

This combination of techniques (BFP-XRF, PGAA, and INAA), was used to analyze mussel homogenates for a total of 43 elements. The compiled results generally showed good agreement. However, some slight differences between techniques were observed for some of the elements. The causes for the differences are currently being investigated. Additional measurements are also in progress to increase the number of elements analyzed by more than one technique. This new multi-element approach using instrumental nuclear and atomic methods will provide the data base needed for environmental evaluation. This multi-element data will allow for the evaluation of source contributions (e.g., pollutant vs. natural environmental contributor) for a realistic assessment of the health of an aquatic community.

5. High Repetition Rate Tunable Laser System for Atomic Spectroscopy  
(26108)

J. R. DeVoe, M. S. Epstein, J. C. Travis, and G. C. Turk

Tunable dye lasers have proven to be valuable excitation sources for the sensitive detection of atomic or molecular species. The dye lasers most widely used for analytical applications are optically pumped by nitrogen, excimer, or Nd:YAG lasers, and furnish pulses a few ns long at rates of 10 to 250 Hz and energies from approximately 100  $\mu$ J to 100 mJ. Cu-vapor-laser-pumped dye lasers provide pulse energies near the lower end of this range ( $\sim$ 100  $\mu$ J), but at a 5-kHz repetition rate, thus providing average power competitive with high energy pulsed lasers or with continuous wave lasers. A 10-W Cu-vapor laser has been acquired to explore several anticipated advantages of this energy delivery mode. Among these advantages is increased photo-excitation efficiency, since the ratio of photons absorbed to incident photon flux diminishes as peak powers approach and exceed optical saturation levels for atomic systems. Because of this improved photon use efficiency, signal averaging time to achieve a given signal-to-noise ratio is less than for a system with higher peak power but equivalent average power. Additionally, for flame applications, every atom passing through the laser interaction volume is illuminated by one or more pulses at typical beam diameters and gas velocities, in spite of the low ( $2 \times 10^{-4}$ ) optical duty factor.

A suitably modified frequency-doubled dye laser pumped by the Cu-vapor laser was used for preliminary laser-enhanced ionization (LEI) and laser-induced fluorescence (LIF) studies in flames. For the present configuration of the laser, LIF is the more sensitive method, and studies are continuing to compare limits-of-detection and precisions to conventional methods and to LIF with high-powered pulsed lasers. Detection limits for LEI are inflated by electrical interference (RFI) emitted by the Cu-vapor laser and by the inability of a single excitation step to provide a suitably high ionization efficiency.

Future plans for the laser system include completion of the fluorescence study and investigation of the application of the Cu-vapor laser (alone) to the opto-acoustic detection of  $\text{NO}_2$ , with staff in the Gas and Particulate Research Division. The intended application of the laser to LEI could be further pursued by acquisition of a recently-announced dye laser optimized for Cu-vapor laser pumping, to be used in conjunction with the presently-used dye laser for stepwise LEI. The resulting two-color laser system would then be suitable for future application to high-repetition rate resonance ionization mass spectrometry (RIMS), with inherently less RFI than the LEI application due to the shielded detector.

6. Development of a High Accuracy Spectrometer for Laser-Enhanced Ionization (26108)

F. C. Ruegg, J. C. Travis, and G. C. Turk

As the utilization of Laser-Enhanced Ionization spectrometry (LEI) for trace metal analysis has increased, the need has arisen to develop an LEI spectrometer for routine use rather than for research. Toward that end, our goal is to use a micro-computer to control and/or monitor critical experimental variables, and to collect, store, display, and process data.

Basic instrumentation for LEI includes a pulsed dual wavelength tunable dye laser, an analytical flame such as used in atomic absorption spectrometry, electrodes that pass current through the flame, and appropriate electronics required to detect the changes in flame current caused by LEI. During the past year we have designed and built a 3 channel "sample-and-hold"/analog-to-digital converter interfaced to a 16 bit microcomputer purchased from the NBS storeroom. This device allows us to store the amplitude of each LEI signal pulse in computer memory, along with the outputs of laser power meters which monitor the pulse-to-pulse fluctuations in laser power of the two laser beams used for LEI. With this information in computer memory, we can test for correlations between LEI signal fluctuations, and fluctuations in power of either, or both, laser beams. When such a correlation is found, the functional dependence of LEI signal on laser power can be determined, and the LEI signal can then be corrected for changes in laser power. We have demonstrated a greater than 3-fold improvement in signal-to-noise ratio utilizing this procedure.

A Fizeau laser wavemeter has also been added to the LEI spectrometer which allows accurate determination of the laser wavelengths. When software development is complete, the fluctuations in laser wavelength will also be monitored and corrected under computer control.

Plans for the near future include further software development for routine analysis, together with improved computer control of laser wavelengths. One goal is the measurement of LEI spectra and display of data in 3 dimensions -- 1st excitation wavelength vs. 2nd excitation wavelength vs. LEI signal. Such spectra will reveal subtle as well as gross interferences, and thus be an aid in assuring accurate analysis.

#### 7. The Determination of Nickel in Petroleum Products Using Laser-Enhanced Ionization Spectrometry (26108)

G. C. Turk

The sensitivity of Laser-Enhanced Ionization spectrometry (LEI) for trace metal analysis has been exploited in helping to solve a difficult chemical analysis problem in the oil industry. The determination of Ni in petroleum process streams is important since Ni can act as a poison when deposited upon the surface of catalysts. The heavy oil flash distillate sample used in this study is typical of petroleum process streams that might be used in hydrotreating reactors. The determination of Ni before and after hydrotreating is a useful monitor of catalytic activity. Conventional methods of analysis have had only marginal success in achieving the precision and accuracy required for this purpose. This work was done in cooperation with Drs. J. D. Webb and A. R. Forster of the Shell Development Company, and Dr. G. J. Havrilla, a former NBS postdoctoral fellow now employed by the Standard Oil Company of Ohio.

The concentration of nickel present in the samples was on the order of 10 ppm, orders of magnitude greater than the LEI detection limit for Ni of 0.08 ppb. This excess sensitivity allows the samples to be highly diluted before aspiration into the flame for LEI analysis. A high dilution factor minimizes the possibility of interferences caused by differences in viscosity between samples and standards. In this case we used a 1 to 100 dilution. The

Ni concentration was determined with a precision of 1.5% (at 95% confidence) and a ratio of signal to background noise of over 700 was obtained. Accuracy of the analysis was verified via an accompanying determination of Ni in SRM 1634b Fuel Oil. The success of this work has led to the construction of LEI spectrometers at both the Shell Development and Standard Oil companies.

8. An Evaluation of the Long-Term Stability of NBS Glass and Thin Metal Film Transmittance SRM's (15310)

R. W. Burke, R. Mavrodineanu, and M. V. Smith

The first glass filter optical transmittance standards, SRM 930, were issued by NBS-CAC in March 1971; the metal-on-quartz filters, SRM 2031, were issued in 1977. To date, more than 1000 sets of SRM 930 and approximately 90 sets of SRM 2031 have been purchased from NBS by various scientific and industrial organizations throughout the world.

At the time of issue, data on the transmittance stability of each set is limited typically to a period of 6 to 9 months. However, through requests from users for NBS to verify or recalibrate these SRM's on an intermittent basis, appreciable data have been acquired on the long-term stability of many sets of SRM 930 that have been in service for more than 10 years and also for some 20 sets of SRM 2031 that have been in use for 3 to 5 years. The maximum change in the transmittance of these SRM's over these time periods has not exceeded 0.5% relative and has averaged 0.3%. For both types of SRM's the transmittance has increased with time.

At the time of certification, the uncertainties in the transmittance values of SRM 930 are 0.5% relative and of SRM 2031, 1%. Long-term stabilities are not specified because they have not yet been rigorously established. Precautionary statements are made, however, that aging and use of these SRM's under adverse conditions could cause the transmittance to change as much as 1% relative in a year. It is therefore reassuring to find that, after multiple years of use, the transmittances of those SRM's that have been remeasured periodically are still within the uncertainties specified on the original certificates.

Studies of the long-term stability of the NBS glass and thin metal film transmittance SRM's in the ultraviolet and visible regions of the spectrum will be continued. Additionally, work is in progress to extend the measurement capability of the high-accuracy spectrophotometer into the near infrared. This extension will provide the instrumentation necessary for establishing the transmittance stability of these SRM's from the current upper wavelength limit of 0.8  $\mu\text{m}$  to 2.5  $\mu\text{m}$ .

9. The Use of the Box Plot to Describe Heterogeneity of Iron Samples (15310)

J. Norris

Current practice in the study of compositional heterogeneity using emission spectroscopy involves the acquisition of large amounts of data representing many selected portions of the intermediate and final forms of

the SRM's. These data include replications of the individual portions that are necessary to provide measures of method precision from which heterogeneity can be estimated. Statistical programs have been used to provide the averages and standard deviations for all sets.

The materials studied may vary from 10 cm square sections of a steel production ingot to the final 3.5 cm diameter rod. Other material types may vary from tapered cones on cast SRM's to 6.4 cm diameter bars for aluminum. Each material has a specific surfacing method; sanding for steels and nickel base, and lathe turning for aluminum, copper and lead. The excitation used samples in an area approximately 6 mm in diameter. Depending on the material, the sample mass is about 2 mg.

Tests as carried out at present may involve between 40 to 80 positions and 160 to 320 individual determinations. It is easier to distinguish between significant variations due to heterogeneity and those due to the inherent variability of the measurement if a box plot is used to present the concentration pattern as a series of x's which represent positions on the metal specimens. This picture dramatically shows measurement precision as a series of closely spaced x's. Material variability is indicated when measurements taken at an adjacent position result in closely spaced x's whose concentrations do not overlap the other measurements. Studies carried out thus far have identified within specimen variabilities that are outside method precision and between specimen variabilities that involved smooth concentration gradients from end to end or discrete steps in concentration resulting from material fabrication.

These plots provide a quick, visual comparison of the patterns developed by different elements in the material. This can be useful in determining which elemental combinations produce heterogeneous concentration distributions and which are to be avoided. Patterns can be frequently observed as combinations of elements such as Mn/S, Nb/C, Ca/Mg, Si/Ti.

Material specifications are continually changing. Current SRM's must represent the best homogeneity available with modern production methods if the SRM is to be useful over its 10 year (plus) intended lifetime.

#### 10. Redetermination of the Atomic Weight of Gallium (15310)

J. W. Gramlich, L. A. Machlan, and L. J. Powell,

The two most recently reported literature values for the atomic weight of gallium, one by mass spectrometry and the other by precise coulometric assay of gallium and arsenic, have significantly different values. To resolve this discrepancy, the atomic weight of a reference sample of gallium (SRM 994) has been determined by combining high precision mass spectrometric methodology with high accuracy chemical assay to provide synthetic calibration mixes of known isotopic composition. The gallium separated isotopes were assayed gravimetrically as  $(C_6H_5)_4AsGaCl_4$  with the small soluble portion being determined by isotope dilution mass spectrometry.

Seven calibration mixes and samples of the SRM were intercompared independently by two analysts using different mass spectrometers. A comparison of the relative isotopic abundance ratios obtained for the calibration mixes with the gravimetrically calculated values produced a correction factor

for sources of systematic error. By applying this correction factor to the relative isotopic ratio obtained for the SRM, a bias free or absolute isotopic abundance ratio was calculated.

The atomic weight calculated from this work is  $69.72307 \pm 0.00007$ . This value is in agreement with the most recently published mass spectrometric value of  $69.723 \pm 0.003$ . Although this work will not change the IUPAC recommended value for the atomic weight of gallium due to reported isotopic variations in commercially available sources, it will provide a highly accurate reference material for this element.

Future plans include determining the atomic weights of: lithium, which is of interest to the nuclear industry, and, via the stoichiometry of  $\text{LiNbO}_3$ , to the solid state industry; nickel, titanium, zinc and germanium, whose atomic weights are the least accurately known, with uncertainties ranging from 1:1500 to 1:6000.

11. Flow-Injection for On-Line Standard Addition Calibration Using a Wavelength-Modulated DCP Spectrometer (15310)

M. S. Epstein

Chemical interferences induced by sample matrix constituents are the primary cause of inaccurate measurements when a direct-current plasma is used as a source for emission spectroscopy. While chemical buffers (i.e., 2 mg/mL Li) can somewhat reduce the magnitude of the interferences, signal enhancement or suppression of up to 30 percent is often observed in buffered samples with complex matrices. Furthermore, the addition of high concentrations of buffer often results in high analyte blanks. The only other alternative is the standard addition procedure, which can be extremely time consuming when a large number of samples must be analyzed. Therefore, we have investigated a flow-injection analysis (FIA) procedure for "on-line" standard addition.

The flow-injection system is peristaltic pump based with 4 channels and the capability to select one of four standard solutions for automatic injection and mixing with the sample stream. While the present system is manually programmed via a terminal, a dedicated microcomputer could easily be used to implement an automatically controlled system. The detection system is an echelle spectrometer equipped with a rapid-scanning refractor plate for background correction. This rapid wavelength modulation system is required when small sample volumes are employed with the flow injection system, since it provides an essentially "simultaneous" background correction.

This system has been employed for standard addition calibration in the determination of Cu in SRM 2673 (Urine) diluted 1:1, Co in SRM 1645 (River Sediment), and Na and Ni in Fuel Oil (1634a,b). Accurate results consistent with results from other analytical techniques were obtained for all analyses with a 50 percent savings in sample/standard preparation and analysis time. Furthermore, sample handling blanks, significant in the determination of Na, were minimized.

Ultimately, the FIA system will be put under complete computer control and interfaced with an autosampling device. This will be necessary for work

involving small samples (<1 mL) where the flow timing parameters are critical. The FIA system will then be used as a transportable sample introduction device for use with ICP, flame emission and flame atomic absorption atomizers, as well as the DCP.

## 12. Speciation of Tributyltin in Seawater (15310)

T. C. Rains

Organotin compounds are frequently used in the production of plastics and in antifouling 'paint' coatings for ship hulls to minimize the accumulation of species such as algae, fungi, bacteria, and mollusks. The toxicity of these chemicals is related to the chemical form of the organotin and some of these compounds may be toxic to humans as well as marine organisms. The goal of this work is to develop a method for analyzing for the various chemical forms of tin including mono, di, and tributyltin species.

The leach rate of these toxic compounds has a significant effect on the service life of the coatings, the antifouling efficiency, and the environmental availability of potentially toxic materials. At the present time the Navy is anticipating a change from copper based antifouling coatings to organotin based coatings which can be formulated to leach at a lower rate with the same degree of antifouling effectiveness. Although this move is expected to result in an extension of the present service life from 24 months to five years or more, little is known about the behavior of these organotin compounds in the marine environment.

Several analytical approaches are currently in use for the determination of Sn(IV), mono-, di-, and tributyltin species in seawater. The basic steps of the generic analytical methodology are the separation of the organotin species, the preconcentration step, and the analytical measurement. Major analytical problems are associated with each of these step which must be resolved to make an accurate determination of total tin and tributyltin. Three of the current analytical approaches are hydride generation, chelation-solvent extraction, and ion-pair liquid-liquid extraction.

The Naval Ocean Systems Center (NOSC) in San Diego has developed a hydride generation technique for the preconcentration and separation of the tin species. The method requires an adjustment of pH of the seawater sample followed by production of the organotin hydrides using  $\text{NaBH}_4$ . The hydrides are collected in a liquid nitrogen trap and then separated on the basis of their relative volatility. The method is slow in that only 8 to 10 samples can be analyzed per day. Also, the accuracy of the method has not been verified by any other analytical technique.

Our task is to evaluate the precision and accuracy of the method used by NOSC for the determination of organotin species in seawater. While the species have been found to be separated by the hydride technique, the recovery was found to be incomplete and variable. Future plans include an investigation of liquid-liquid extraction as a means of separation and preconcentration and modification of the hydride generation method presently being used. Another approach would be to take advantage of the organophilic properties of these organotin species and preconcentrate them on a nonpolar



stationary phase directly or by headspace analysis from seawater. The separation of the species is performed by liquid-phase technique with laser-enhanced ionization spectrometry or electrochemical detection.

13. Physical and Chemical Properties of Aerosols Produced by the Spark Discharge (15310)

R. L. Watters, Jr, R. A. Fletcher, R. L. McKenzie, and J. A. Small

Some of the most advantageous analytical spectrometric techniques involve the direct sampling of solid material. Such an approach eliminates time consuming dissolution procedures and the errors associated with analyte loss and contamination. However, techniques such as optical emission spectrometry, spark source mass spectrometry, and microprobe mass spectrometry, which use direct solid sampling, can exhibit systematic errors due to the combined effects of bias in the sample transport and excitation processes. As a result, each instrumental technique requires calibration standards for each type of sample matrix that is to be analyzed. The key to alleviating this need for standards in every possible matrix is to develop analytical techniques that do not exhibit bias from one matrix to another. When such instrumental techniques consist of a sampling step followed by an excitation step, it is essential that bias in each of these steps be examined separately. To focus on the transformation of sample material from the bulk, we have been examining the physical and chemical properties of aerosols generated by condensation of vapor produced by the spark discharge.

The spark is a useful means of converting solid conducting samples into an aerosol for introduction into an inductively coupled plasma (ICP). Particle size distributions have been measured for pure materials (Fe, Cu, Pb, Al, W, Mo) and the effects of spark repetition rate and peak current have been recorded. The aerosol produced is nearly monodisperse with a mean diameter of about 0.1  $\mu\text{m}$ . A few larger particles (-5-10  $\mu\text{m}$ ), which are nearly spherical, have also been detected using scanning electron microscopy (SEM). The smaller particles form loosely bound chains and clusters when collected on screens for SEM analysis. These chains and clusters apparently break apart in the mobility analyzer, which registers the 0.1- $\mu\text{m}$  fundamental aerosol units. Further experimentation is needed to determine whether the clusters are formed in the aerosol stream or are caused by the electrostatic collector.

Preliminary x-ray analysis of the chains and spheres using the analytical electron microscopy (AEM), has indicated a compositional difference between the chains and the spheres. To quantify the chemical composition of the collected aerosol, a series of brass SRM's has been examined to determine Zn/Cu ratios for the particle size groups separated by a two-stage filter collector. These stages separate the submicrometer from the 8-10  $\mu\text{m}$  group. Particles on each filter were dissolved and analyzed by ICP. Initial results indicate a bias in the Zn/Cu ratio for particles collected by both filter stages. These data also indicate that the mobility analyzer count of a small fraction of the aerosol stream can be used to provide a ratio for the mass balance of total material sampled. At present, no mass flow rate is used and the spark-ICP analytical instrument must analyze for every element in the sample and normalize the data to 100%, thereby substantially increasing the error. Additional measurements of this type are in progress.

The continuation of this work will include using SEM to examine the filters to ascertain the degree of cluster formation. This will provide a comparison between the previously measured characteristics of the aerosol sampler and the actual size ranges collected in these experiments. The studies will include other alloys to examine the effects of alloy physical properties and chemical composition on sampling.

The sampling and collection schemes in the present experiments will be used to assess the feasibility of real-time analysis of ambient aerosols. Where results indicate analytical promise, sampling devices such as the spark will be coupled to the ICP, DCP, or chemical flame as excitation sources for optical emission analytical spectrometry with the ultimate objective of providing an analysis technique free from matrix effects.

14. Characterization of Autoionizing Levels in Beryllium with Resonance Ionization Mass Spectrometry (15310)

J. D. Fassett, L. J. Moore, C. W. Clark, W. W. Smith, and  
T. B. Lucatorto

Autoionizing levels are discrete electronic levels of an element that are at energies greater than the ionization potential. In general, autoionizing levels of most elements are not well characterized or understood. Resonance ionization mass spectrometry (RIMS) has the promise of sensitively detecting these levels. The single or multiple absorption of photon(s) from a discrete electronic level below the ionization continuum results in an enhancement in the ionization probability of the element, since the cross-section for absorption is greater to this autoionizing level than into the surrounding continuum. The excited atom spontaneously loses an electron to become an ion. We have investigated Be because of the extensive theoretical attention that has been given to the treatment of its autoionizing states. Since Be is the simplest atom that has two electrons outside a closed shell, it is the prototype for the study of electron correlation. There have been at least 8 theoretical estimates of the position of the  $1s^2 2p^2 \ ^1S_0$  autoionizing level of Be which range from 1800-7100  $\text{cm}^{-1}$  above the ionization potential. We initiated experiments to establish the position of this autoionizing level.

A resonance line has been observed at 262.5 nm that we ascribe to the  $1s^2 2p^2 \ ^1S_0$  autoionizing level of Be for the following reasons: (1) the power dependence of the ionization is squared, indicating a 2-photon process; (2) the polarization dependence of the transition,  $\Delta J=0$ , is correct; and, (3) the line width and position are theoretically tenable. The experimental position, 1004  $\text{cm}^{-1}$  above the ionization potential, is 800  $\text{cm}^{-1}$  lower than the closest theoretical calculation. If the intershell correlations of the K and L shells are included in this theoretical calculation, the experimental and theoretical energies differ by only 100  $\text{cm}^{-1}$ .

In the preliminary experiments in which RIMS of Be was demonstrated, a series of low intensity lines was observed in the spectra. These lines have been identified also as autoionizing transitions, in this case representing 3-photon transitions resonantly enhanced by a near-lying 2-photon transition. These lines are transitions from the  $1s^2 2s^2$  ground state to the  $1s^2 2s nd$

Rydberg series where we observe  $n=5-15$  of this Rydberg series. These high-lying members of this Rydberg series similarly have never been experimentally observed.

Although this study of Be is experimentally complete, the observation of 2- and 3-photon transitions to autoionizing levels promises to explain many of the previously unassignable spectroscopic features observed in RIMS spectra. Furthermore, autoionizing levels could be used in schemes to increase the sensitivity of the ionization process by making one of the photons in a multiphoton absorption process resonant between an autoionizing level and a discrete level below the ionization continuum. This work has broadened our basic understanding of both the resonance ionization mass spectrometry technique and atomic physics.

15. The Determination of Iron in Serum and Water by Resonance Ionization Isotope Dilution Mass Spectrometry (15310)

J. D. Fassett, L. J. Powell, and L. J. Moore

Resonance ionization mass spectrometry (RIMS) is a relatively new technique that combines optical spectroscopy with mass spectrometry. The technique exploits lasers to selectively and efficiently ionize gas phase atomic species. When the laser is tuned to a discrete resonant electronic transition of an element, the ionization probability increases many-fold due to the stepwise absorption of photons. Most of the initial applications of RIMS have been made with modified thermal ionization mass spectrometers (TIMS). RIMS can be applied to TIMS measurement problems where lack of sensitivity (failure to produce ions) and/or non-selectivity (isobaric interferences) result in fundamental limitations. The RIMS potential is demonstrated by its application to the accurate analytical determination of iron, an element for which thermal ionization is particularly insensitive.

Resonance ionization mass spectrometry has been used in conjunction with isotope dilution to determine the iron content of SRM 909 (Human Serum) and SRM 1643b (Trace Elements in Water). Iron was thermally vaporized from a filament at 1250 K. We have computed from the Saha-Langmuir expression that the  $\text{Fe}^0/\text{Fe}^+$  ratio is  $\sim 10^{12}$  at 1250 K, and from this we estimate that the RIMS system is  $10^7$  more sensitive than TIMS. This estimate includes losses from the duty cycle of RIMS at  $\sim 10^{-5}$ . A one-wavelength, two-photon ionization scheme was employed utilizing UV radiation at 283.6 nm provided by a Nd:YAC pumped dye laser with frequency doubling. The mass spectrometer used was a 15 cm radius magnetic sector instrument of NBS design. The linearity of the detection system was verified by the determination of the  $^{57}\text{Fe}/^{56}\text{Fe}$  ratios in a set of gravimetrically prepared isotopic calibration mixes, over a  $^{57}\text{Fe}/^{56}\text{Fe}$  ratio range of  $\sim 750$ . The precision and accuracy of the measurements were typically 2-3 percent. The mass spectrometric loading blank is presently the limiting source of error. The concentration and uncertainty (95% confidence limits) of the certified values of Fe in SRM 909 are  $1.94 \pm 0.29$   $\mu\text{g/g}$  and in SRM 1643b are  $99.2 \pm 8.3$   $\text{ng/g}$ .

This work represents the first isotope dilution application using RIMS. Plans for extending this research include an evaluation of systematic biases involved in the ionization and measurement processes, with the intention of developing highly sensitive and selective multielement isotope dilution capabilities at precisions, and accuracies well within one percent. This

evaluation will require a better understanding of the resonance ionization process itself, particularly with respect to the possible effects of isotopic discrimination. The accurate measurement of pulsed ion currents using a time-gated detection system will be investigated. One effective application of this research could be the determination of chromium-vanadium-titanium trace element mixtures for which chemical separation of isobaric interferences is difficult and for which the sensitivity and elemental selectivity of RIMS would be ideally suited.

## 16. High Precision Isotope Ratio Measurements of CO<sub>2</sub> (15310)

I. L. Barnes, P. Morales, J. Gramlich, and W. A. Bowman, III

The technique of isotope dilution mass spectrometry (ID/MS) has developed during the past fifteen years into the definitive method for the analysis of trace elements in solid samples. As a logical extension of this technique, this project was intended to develop the instrumentation and methodology for the determination of traces of compounds of carbon, oxygen, nitrogen, and sulfur in various gas mixtures by ID/MS. The determination of the concentration of carbon dioxide in nitrogen and air was selected as the first analytical problem with application to the certification of a series of gas Standard Reference Materials.

A new and unique 30 cm radius, 90° deflection mass spectrometer designed for high precision gas analysis was constructed. Salient features include an electron impact ionization source, a new ultrastable emission regulator, a triple, deep-Faraday-cup collector, and a direct ratio reading measurement system. The instrument is automated and controlled by a small computer. A dual gas sample storage and introduction system and an isotope dilution mixing line were also constructed.

Initial measurement precision has been quite satisfactory. As an example, we obtain delta (parts per 1000) <sup>18</sup>O values of  $+0.3892 \pm 0.0006$  and  $+2.1993 \pm 0.0005$  for two CO<sub>2</sub> standards which may be favorably compared with the best recently published values of  $+0.389 \pm 0.001$  and  $+2.199 \pm 0.004$ . Similar precision has been obtained in the measurement of the isotopic ratios of 7 other standard materials commonly used in the light stable isotope community. Isotope dilution measurements are currently being made on samples of a research cylinder of CO<sub>2</sub> in air. When complete, a series of measurements will be made on a series of SRM samples of CO<sub>2</sub> in nitrogen.

It is planned, in future work, to measure a series of samples at very different concentrations, to start a redetermination of the atomic weight of oxygen, and to explore the possibility of extending the system to compounds of nitrogen and sulfur.

## 17. Certification of Nuclear Isotopic Standard Reference Materials (15310)

J. W. Gramlich, L. A. Machlan, B. S. Carpenter, R. R. Greenberg, and J. R. Moody

Reference materials with accurately known isotopic compositions are essential for instrument calibration in the nuclear industry to assure the safeguarding and accountability of nuclear materials. Two sets of uranium isotopic Standard Reference Materials have been certified for isotopic

composition; one set for use in destructive assay (DA) by mass spectrometry, and the other set for non-destructive assay (NDA) intended for gamma spectrometry calibration.

The destructive assay material consists of a renewal of three of a series of 17 uranium isotopic standards, ranging from depleted to highly enriched  $^{235}\text{U}$  abundance. The renewal SRM's U-030a, U-020a and U-005a have been certified with an accuracy a factor of two better than previously certified uranium isotopic standards. The decreased uncertainty in these measurements is the result of improved analytical methodology, both in the chemical assay and the mass spectrometry.

The development of a Standard Reference Material for non-destructive assay represents a cooperative effort between NBS, The Commission of the European Communities, Central Bureau for Nuclear Measurements, Geel, Belgium, and the U.S. Department of Energy, New Brunswick Laboratory, Argonne, Illinois. This Standard Reference Material (SRM 969) "Uranium Isotopic Standard Reference Material for Gamma-Ray Spectrometry Measurements" is intended for use in the calibration and evaluation of counting procedures for the non-destructive determination of the  $^{235}\text{U}$  isotope abundance in uranium bulk materials. SRM 969 consists of a set of five different  $\text{U}_3\text{O}_8$  powders with  $^{235}\text{U}$  abundances of 0.31, 0.71, 1.94, 2.94 and 4.46 weight percent, together with an empty container. The empty container is provided for measuring uranium bulk material of unknown  $^{235}\text{U}$  abundance. SRM 969 was prepared as a set to permit accurate enrichment measurements on low enriched uranium materials by testing the theoretically expected linear relationship between  $^{235}\text{U}$  abundance and the counting rate of the 185.7 KeV gamma-ray of  $^{235}\text{U}$ . Each SRM sub-unit is made up of 200g of  $\text{U}_3\text{O}_8$  powder sealed in a tamper proof aluminum can. Each container was manufactured to rigid specifications and thoroughly tested. SRM 969 will be issued in Europe by the Central Bureau of Nuclear Measurements as Reference Material EC 171.

The issuance of these two sets of uranium isotopic SRM's is expected to substantially improve, on an international scale, accountability measurements in the nuclear industry.

18. Determination of Trace-Level Cr(VI) in the Presence of Cr(III) and Fe(III) by Voltammetric Flow-Injection Analysis (15310)

K. W. Pratt and W. F. Koch

The toxicity of Cr(VI) in natural waters is much greater than that of Cr(III). Hence, the oxidation state specific determination of Cr(VI) at trace levels is of significant interest in environmental analyses. Most trace-level techniques are element-specific but do not differentiate among different oxidation states of a given element. A preliminary separation of Cr(VI) from Cr(III) is thus required for determinations based on these element-specific methodologies.

Flow-injection analysis with amperometric detection provides a simple, inexpensive method for the determination of Cr(VI) at trace levels in the presence of Cr(III). Two significant improvements in this technology have been accomplished. First, the vibrating wire electrode (VWE) has been applied as an amperometric detector for the determination of Cr(VI) by flow-injection analysis. Use of the VWE has effected a 10-to 20-fold

increase in the sensitivity of the determination. This improvement is a direct consequence of the increased rate of mass transport resulting from the vibration of the electrode. Detection limits for Cr(VI) at the VWE are at the ppb level. The second improvement is the elimination of the interference of Fe(III) in the voltammetric determination of Cr(VI) by using  $H_3PO_4$  instead of HCl or  $H_2SO_4$  as the supporting electrolyte. The Fe(III) in the sample is complexed by the  $(HPO_4)^{2-}$ , and the Fe(III)- $(HPO_4)^{2-}$  complex is not reduced at the electrode at the potential used for the detection of Cr(VI). Substitution of  $H_4P_2O_7$  for  $H_3PO_4$  has permitted a still broader range of potentials to be used for the amperometric detection of Cr(VI) without interference from Fe(III). Direct determinations of Cr(VI) without prior separation of Fe(III) and Cr(VI) are thus possible for the first time in matrices typically encountered in natural waters.

Future directions for this project include application of this methodology to the determination of Cr(VI) in marine and environmental samples. In addition, the electrocatalysis of the reduction of Cr(VI) at Pt and Pd electrodes by adsorbed iodine will be studied, with a view toward optimizing the reproducibility of response of the electrodes. Application of the VWE to determinations of other electroactive species by flow-injection analysis are also anticipated. It is expected that this procedure will permit the determination of the various chemical forms of elements in solution.

19. The Measurement of pH and Acidity in Rainwater: Development of a Research Material/Simulated Rainwater (15310)

W. F. Koch, G. Marinenko, and Y. C. Wu

The research effort to provide a meaningful basis and quality assurance for analytical measurements in acid rain studies has continued this year with noteworthy advances. This long-term project has been in support of the National Acid Precipitation Assessment Program (NAPAP) at the request of the Environmental Protection Agency (EPA). It encompasses the evaluation of existing methodologies for analytical measurements, the development of improved measurement procedures which address the unique characteristics of acid rain, and the development and characterization of stable, homogeneous research materials in solution form to aid in the analysis of rainwater. The primary focus of this year's activities has been in the measurements of pH and acidity.

A round-robin exercise was conducted early in the year to test the efficacy of using dilute solutions of a strong acid as working standards for pH measurements in acid rain. Twelve laboratories, distributed among government, industry and academia, voluntarily participated in this test. The results prove conclusively that the residual liquid junction potential can seriously bias pH measurements and that the use of matrix-matched pH standards will significantly reduce this bias. These matrix-matched pH standards should be consistent with the National pH scale as maintained through the NBS Standard Reference Materials (SRM's) pH buffers so that measurements of pH be as thermodynamically meaningful as possible and to avoid confusion caused by multiple pH scales. To this end, a Research Material, RM 8409, Simulated Rainwater, has been developed and is now available. RM 8409 is a set consisting of two 50-mL solutions in polyethylene bottles. The pH values of the solutions have been established through the use of potentiometric hydrogen cells without liquid junction and confirmed by coulometric titration

and ion balance calculations. Guidelines for the measurement of pH in rainwater have been developed which incorporate RM 8409. This recommended procedure has undergone statistical ruggedness testing to evaluate the effects of various parameters on the measurement. The parameters tested include temperature, stirring, equilibration time, dilution, immersion depth of electrodes, and the addition of neutral salts. The effect of carbon dioxide on the pH value of rainwater will be evaluated in the future. The effect of carbon dioxide on the value of the acidity of rainwater has been investigated and found to be significant, particularly in rainwater of low acidity. It has been recommended that rainwater be deaerated by purging with nitrogen or argon prior to titration and that the titration be carried out either by the method of Gran or by potentiometric titration to the inflection point. A great deal of research remains to be done on quantifying the effects of carbon dioxide due to its complex equilibria in solution, its slow reaction kinetics, and its easily perturbed partial pressure.

Work leading to an SRM for rainwater will be initiated this year. Recommended procedures for the measurements of pH and acidity will be issued as an integral part of the certificate. This will represent the first of a series of matrix-specific pH standards. (Future standards will include seawater and biological fluids.) Also, it will be the first aqueous SRM for anions and for specific conductance. The acid rain project will expand this year to begin investigating the needs for standards and analytical procedures in dry deposition, focusing on the assessment of analytical errors and on the stability of solutions containing inorganic species at the  $10^{-7}$  g/g and below levels.

## 20. Uranium and Sulfur Isotopic Tracers in the Environment (15310)

J. D. Fassett, W. R. Kelly, and P. J. Paulsen

Contamination of the atmosphere can occur as the result of nuclear accidents and can be sensitively monitored by using high precision mass spectrometry. In collaboration with the DOE-Environmental Measurements Laboratory, we have determined the  $^{235}\text{U}/^{238}\text{U}$  ratios in several air filters that were flown at high altitudes and that were intended to intercept debris from the Soviet reconnaissance satellite, Cosmos 1402, which reentered the atmosphere over the Indian Ocean on January 24, 1983. Cosmos 1402 was a four-ton space craft powered by 55 kg of enriched  $^{235}\text{U}$  and was launched on August 30, 1983. This type of satellite normally operates for 6-7 months before being boosted to a stable orbit expected to last 1000 years. Cosmos 1402 had been turned off December 28, 1983, and the orbital boost apparently failed in this case.

The analytical procedure used was as follows: approximately 5 g of filter is spiked with a small quantity (10-20 pg) of  $^{233}\text{U}$  spike and wet ashed using a mixture of  $\text{HClO}_4/\text{HNO}_3$ . The U is separated using anion exchange chromatography [1]. This procedure separates U in pure form and with a high yield for mass spectrometric determination.

The three filters that have been analyzed thus far contained about 200 pg/g of  $^{238}\text{U}$  and showed enrichments of  $^{235}\text{U}$  of 25% above blank filter material. The data indicate that Cosmos 1402 debris was intercepted. This information will be used by EML to plan future flights.

An investigation has been initiated on the use of sulfur isotopes to trace SO<sub>2</sub> emissions from coal-fired power plants. There are two possible approaches in the use of sulfur isotopes for this purpose. One is to use the natural variability in the isotopic composition to identify the source of emissions and the other is the intentional release of an artificially enriched isotope of sulfur from a particular power plant. The former approach is being tried using size fractionated aerosol samples obtained from the Deep Creek Lake Experiment carried out in the summer of 1983. The enriched isotope approach may be attempted in the near future using centrifuge-enriched <sup>34</sup>S. For this approach to succeed, the natural fractionation effects will need to be differentiated from the intentional <sup>34</sup>S enrichment. One way to do this is to use the <sup>32</sup>S/<sup>33</sup>S ratio as an internal standard to remove natural and instrumental fractionation effects from the measured <sup>34</sup>S/<sup>32</sup>S ratio. This approach has yet to be demonstrated for S, but it is planned for the near future.

[1] W. R. Kelly and J. D. Fassett, Anal. Chem. 55, 1040 (1983).

## 21. Standard Reference Materials

### B. I. Diamondstone

As in past years, the Division has put considerable effort into the process of certifying Standard Reference Materials (SRM's). The combination of research and certification analyses account for approximately thirty percent of the total staff effort. The expertise required to successfully implement this program comes from all of the groups in the Division. Nearly all members of the Division participate in one or more aspects of acceptance testing, homogeneity evaluation, or accurate analysis, leading to the certification of inorganic constituents in potential SRM materials.

Listed below are seven different areas of research that were funded by the Office of Standard Reference Materials during the past year. This portion of the STRS OSRM funding is intended for the preliminary research necessary to develop the methodologies required for the actual production of SRM's. The actual certification for chemical composition on a marketable standard is carried out as a WCF project.



STRS Projects Supported by OSRM During FY 84

<u>Task</u>	<u>Description</u>	<u>Effort, SY</u>
Gases in Metals	Research leading to the developmment of methods and procedures for certifying oxygen, hydrogen, nitrogen, and carbon in a variety of metal matrices.	0.5
Particle Size Fraction	Research leading to the following: 1) evaluation of candidate materials and loading procedures for the production of a natural matrix material on filter media; 2) evaluation of the relationship of the chemical composition of SRM 1648 to its particle size distributions.	0.35
Cast/Wrought Effects	Research leading to the evaluation of differences in optical emission behavior of cast and wrought SRM's.	0.20
Aqueous Electrolytic Conductance Stds	Research leading to an understanding of the fundamentals of conductivity measurements. Investigate feasibility of producing aqueous conductivity SRM's.	0.25
pH Measurements	Research leading to the development of improved methods for making accurate pH measurements	0.20
Noble Metals	Research leading to the development of prototype SRM's for the certification of noble metals on silica.	0.20
Complex Matrices	Research leading to the development of methods for the measurement of trace elements in biological materials and the preparation and evaluation of a Rainwater Research Material.	0.70
		2.4

Listed below are approximately 75 different SRM's that were analyzed for as many as 30 different elements. These materials included metals, fossil fuels, body fluids, foods, nuclear materials, biologicals, and glasses.

Standard Reference Materials Analyzed During FY 84  
and Division Effort in Staff Years

<u>SRM Number</u>	<u>Title</u>	<u>Effort, SY</u>
2122,2123,2124	Spectrometric Solution Stds	0.5
1618	V-Ni-S in Residual Fuel Oil	0.2
2679a	Quartz on Filter Media	0.3
679	Trace Elements in Brick Clay	0.5
1634b	Trace Elements in Fuel Oil	0.7
650,651,652	Unalloyed Titanium	0.25
1632b	Trace Elements in Coal	0.8
185f	KHP (pH)	0.2
2185	KHP (pD)	0.2
44f	Hi-Purity Aluminum	0.03
1818	Cl in Rerefined Oils	0.05
15h	Plain Carbon Steel	0.01
2033	Potassium Iodide Stray Light Std	0.1
2135	Silicon Wafers	0.01
930d	Glass Filters for Spectrometry	0.3
2031	Metal On Quartz Filters	0.3
2400,2400a,2401,2401a,2402	White Irons	0.01
1290,1290a,1291,1291a,1292	White Irons	0.01
1218	Silicon Steel	0.01
1003a	Glass Spheres	0.02
1761-1767	Low Alloy Steels	0.2
394,396,398,400	Copper Benchmarks	0.2
955	Porcine Blood	0.1
2670	Trace Elements in Urine	0.2
173c	Titanium Base Alloys	0.03
1832	XRF Thin Films	0.03
359	Zircaloy	0.15
33e	Low Alloy Steel	0.02
1255a,1256a,1240,1241	Aluminum Alloy	0.1
2415	Lead	0.1
1761-1767	Low Alloy Steel	0.6
c1253	Copper Benchmarks	0.1
1572	Citrus Leaves	0.1
976,978a,987.	Isotopics	0.04
1577	Bovine Liver	0.1

6.7

Existing and newly developed methodologies were successfully used to issue three environmentally important SRM's during the past year. These materials, milk, urine, and serum, required nearly a dozen separate analytical techniques for certification. Additional elements in these materials will be added to the certification list during the next year. In the metals area, a number of new materials have been certified for oxygen, hydrogen, and nitrogen. Analytical procedures for determining these gases in metals have not been available at NBS during recent years. In addition, uncertified elements in existing SRM's are continually being certified as new analytical techniques are developed and values for previously certified elements in existing SRM's are periodically checked and updated as new, more accurate

methods become available. Before the year is over, nine sets of aqueous standards will be available for use with spectrometric techniques such as AAS, ICP, DCP, and spectrophotometry.

It is anticipated that next year we will see the issuance of additional metal samples certified for hydrogen, oxygen, and nitrogen content and work will commence on lead and aluminum standards. Work will begin on a number of other new and reissued SRM's, including limestone, flint and plastic clays, rice and wheat flour, and sulfur in kerosene.

C.     Outputs and Interactions  
       (Inorganic Analytical Research Division)

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- Fassett, J. D., Travis, J. C., and Moore, L. J., "Thermal Atomization Sources and Resonance Ionization Mass Spectrometry (RIMS)," Proc. of the SPIE Symposium East '84, in press.
- Greenberg, R. R., "Radiochemical Procedures Used for Improved Low-Level Determinations of Critical Elements in Biological Materials," Atomkernenergie-Kerntechnik, in press.
- Greenberg, R. R. and Carpenter, B. S., "High Accuracy/High Precision Determination of U-235 in Nondestructive Assay Standards by Gamma-Ray Spectrometry," Proc. Fifth Intl. Conf. on Nuclear Methods in Environmental and Energy Research, in press.
- Greenberg, R. R., Fleming, R. F., and Zeisler, R., "High Sensitivity Neutron Activation Analysis of Biological/Environmental Standard Reference Materials," Environ. International, in press.

- Kelly, W. R., "On the Precise and Accurate Determination of the  $^{241}\text{Pu}$  Half-Life by Mass Spectrometry," in press.
- Kelly, W. R. and Paulsen, P. J., "Precise and Accurate Determination of High Concentrations of Sulfur by Isotope Dilution Thermal Ionization Mass Spectrometry," in press.
- Kelly, W. R. and Paulsen, P. J., "Determination of Sulfur in NBS Coals by Isotope Dilution Thermal Ionization Mass Spectrometry," in press.
- Kingston, H. M. and Greenberg, R. R., "An Elemental Ratioing Technique for Assessing Concentration Data from a Complex Water System," *Environ. International*, in press.
- Kingston, H. M., Paulsen, P. J., and Lambert, G. M., "The Determination of Selenium and Tellurium in Stainless Steel, White Cast Iron, and Nickel Base Alloy Standard Reference Materials by Isotope Dilution Spark Source Mass Spectrometry," *Applied Spectroscopy*, in press.
- Koch, W. F., Marinenko, G., and Wu, Y. C., "The Development of Reference Materials for Acid Rain Research," *Environ. International*, in press.
- Lutz, G. J., Rook, H. L., and Lindstrom, R. M., "Determination of I-129 at Natural Levels by Thermal Neutron Activation Analysis," *Journal of Trace and Microprobe Techniques*, in press.
- May, J. C., Rains, T. C., Mainethal, E. J., Bridgley, G. N., and Progan, J. J., "Survey of the Concentration of Eleven Metals in Vaccines, Allergenic Products, Toxides, Blood, Blood Products and Other Biological Products," *J. Biol. Stand.*, in press.
- Moody, J. R., "New Developments in Laboratory Design in the U.S.A.," in *Design, Construction and Refurbishment of Laboratories*, R. Lees and A. F. Smith, eds., Ellis Horwood and Sons, Chichester, UK, in press.
- Moody, J. R., "Sampling, Storage, and Handling of Materials for Trace Element Analysis," in *Sample Preparation Technology - Volume 3*, Zymark Corp., Hopkinton, MA, in press.
- Moore, L. J., "Stable Isotope Measurements with Thermal and Resonance Ionization Mass Spectrometry," *ACS Advances in Chemistry Series, Stable Isotopes in Nutrition*, in press.
- Moore, L. J., Kingston, H. M., Murphy, T. J., "The Use of Isotope Dilution Mass Spectrometry for the Certification of Standard Reference Materials," *Environ. International*, in press.
- Powell, L. J. and Murphy, T. J., "The Determination of Atomic Weights at NBS--The Case of Silver and Its Impact on the Faraday," *Chem. Tech.*, in press.
- Pratt, K. W., "Chronoamperometric Determination of Diffusion Layer Thicknesses at Hydrodynamic Electrodes," *Anal. Chem.*, in press.



- Rains, T. C., Watters, R. L., Jr., and Epstein, M. S., "Application of Atomic Absorption and Plasma Emission Spectrometry for Environmental Analysis," Environ. International, in press.
- Stone, S. F. and Zeisler, R. L., "Evaluation of Biological Samples for Specimen Banking and Biomonitoring by Nuclear Methods," Proc. of Fifth International Conference on Nuclear Methods in Environmental and Energy Research, April 2-6, in press.
- Wise, S. A. and Zeisler, R., "The Pilot Environmental Specimen Bank Program," Environ. Sci. Technol., in press.
- Downing, R. G., Fleming, R. F., Maki, J. T., Simons, D. S., and Stallard, B. R., "Near-Surface and Interfacial Profiling by Neutron Depth Profiling (NDP) and Secondary Ion Mass Spectrometry (SIMS)," Thin Solid Films, submitted for publication.
- Downing, R. G., Maki, J. T., and Fleming, R. F., "Application of Neutron Depth Profiling to Microelectronic Materials Processing," Special Proceedings of the Industrial Chemical Division Session for the 187th National Meeting of the American Chemical Society, L. A. Casper, ed., submitted for publication
- Marinenko, G. and Koch, W. F., "A Critical Review of Measurement Practices for the Determination of pH and Acidity of Atmospheric Precipitation," Environ. International, submitted for publication.
- Moore, L. J., Fassett, J. D., and Travis, J. C., "Systematics of Multielement Analysis Using Resonance Ionization Mass Spectrometry and Thermal Atomization," submitted for publication.
- Riley, J. E., Jr., Mitchell, J. W., Downing, R. G., Fleming, R. F., Lindstrom, R. M., and Vincent, D. M., "Materials Analysis Using Thermal Neutron Reactions: Applications," Journal of Solid State Chemistry, submitted for publication.
- Tanaka, T., Marinenko, G., and Koch, W. F., "Further Developments in the High-Precision Coulometric Titration of Uranium," submitted for publication.
- Wilson, S. R., Paulson, W. M., Gregory, R. B., Krause, S. J. Gresset, J. D., McDaniel, F. D., and Downing, R. G., "Properties of Ion Implanted Polysilicon Layers Subjected to Rapid Thermal Annealing," Journal of the Electrochemical Society, submitted for publication.
- Wu, Y. C., Koch, W. F., and Marinenko, G., "A Special Report on the State of the NBS pH Standards," Anal. Chem., submitted for publication.

## 2. Talks

Fassett, J. D., Travis, J. C., and Moore, L. J., "Resonance Ionization Mass Spectrometry of Iron--Quantitative Aspects," 26th Ann. Conf. on Analytical Chemistry in Energy Technology, Knoxville, TN, October 4, 1983.  
Invited

Kelly, W. R., "Enriched Rare Earth Isotopes as Tracers of Aerosol Particulate Emissions from Coal-Fired Power Plants," Electric Power Research Institute, Palo Alto, CA, October 4, 1983.

Koch, W. F., "Measurement of pH: Liquid Junction Potentials," U.S. Environmental Protection Agency, Research Triangle Park, NC, October 12, 1983.  
Invited

Watters, R. L., Jr., Norris, J. A., Small, J. A., McKenzie, R. L. and DeVoe, J. R., "Material Transport in Atomic Spectrometry," 26th Conference on Analytical Chemistry in Energy Technology, Knoxville, TN, October 12, 1983.

Fleming, R. F., "Elemental Depth Profiling with a Thermal Neutron Beam," Department of Chemistry seminar, University of Maryland, College Park, MD, October 14, 1983.

Fassett, J. D., "Recent Developments in Resonance Ionization Mass Spectrometry," Washington Area Mass Spectrometry Discussion Group, October 17, 1983. Invited

Fleming, R. F., Langland, J. K., and Downing, R. G., "Elemental Depth Profiling with a Thermal Neutron Beam," Conference on the Use and Development of Small and Medium Power Reactors, Cambridge, MA, October 17, 1983.

Greenberg, R. R., "Radiochemical Procedures for Improved Low-Level Determination of Critical Elements in Biological Materials," International Symposium on the Use and Development of Low and Medium Flux Research Reactors, Cambridge, MA, October 17, 1983.

Rains, T. C., "State of the Art of Atomic Absorption Spectrometry," 3rd NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, October 25, 1983.

Watters, R. L., Jr., "Atomic Emission Spectrometry Using the Inductively Coupled Plasma (ICP) Technique," 3rd NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, October 25, 1983. Invited

Gramlich, J. W., "Inorganic Mass Spectrometry Applications," 3rd NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, October 27, 1983. Invited

Deal, E. C., "Determining the Provenance on Works of Art and Comparative Samples by Lead Isotopic Ratio Analysis," 3rd NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, October 28, 1983. Invited

- Burke, R. W., "Standardization of Spectrophotometers and Spectrofluorometers," American Association for Clinical Chemistry, Michigan Section, Pontiac, MI, November 3, 1983. Invited
- Stone, S. F., "Trace Multielemental Analysis of Banked Biological Samples," Analytical, Nuclear and Environmental Chemistry Division, University of Maryland, College Park, MD, November 5, 1983.
- Gramlich, J. W., "Determination of Atomic Weights at NBS," 883rd Meeting of the Chemical Society of Washington, National Bureau of Standards, Gaithersburg, MD, November 10, 1983. Invited
- Downing, R. G., Maki, J. T., Fleming, R. F., Stallard, B. R., and Simons, D. S., "Near-surface and Interfacial Profiling by Neutron Depth Profiling (NDP) and Secondary Ion Mass Spectroscopy (SIMS)," Thin Films and Interfaces Symposium, Materials Research Society, Boston, MA, November 14, 1983.
- Fleming, R. F., "Neutron Depth Profiling for Materials Analysis," Department of Nuclear Engineering seminar, University of Maryland, College Park, MD, November 17, 1983
- Olin, J. S., Balckman, M. J., and Jornet, A., "Elemental Analysis of Spanish-Colonial Majolica to Determine Provenience," Seventeenth Annual Meeting of the Society for Historical Archaeology, Williamsburg, VA, January 5, 1984.
- Barnes, I. L. and Deal, E. C., "The Use of Lead Isotope Ratios for the Determination of the Provenience of Ancient Objects," Conservation Analytical Laboratory seminar, Smithsonian Institution, Suitland, MD, January 10, 1984. Invited
- Kelly, W. R., "Enriched Rare Earth Isotopes as Tracers of Aerosol Particulate Emissions from Coal-fired Power Plants," Department of Energy, Germantown, MD, January 12, 1984.
- Travis, J. C., "Laser-Enhanced Ionization Spectrometry," Department of Chemistry seminar, The Catholic University of America, Washington, DC, February 3, 1984.
- Ehrstein, J. R., Downing, R. G., Stallard, B. R., Simons, D. S., and Fleming, R. F., "Comparison of Depth Profiling of B-10 in Silicon by Spreading Resistance Profiling, Secondary Ion Mass Spectrometry, and Neutron Depth Profiling," Third Symposium on Semiconductor Processing, San Jose, CA, February 10, 1984.
- Moody, J. R., "Characterization of Fluoropolymers and Other Polymers for Trace Element Contamination," E.I. Du Pont Co., Wilmington, DE, February 13, 1984. Invited
- Watters, R. L., Jr., "Recent Advances in Atomic Spectrometry and Microanalysis," Society for Applied Spectroscopy, New York Section, February 14, 1984. Invited

- Kelly, W. R., "Analytical Techniques for Sulfur Isotope Measurement," DOE Workshop on Sulfur Isotopes in Environmental Studies, Department of Energy, Germantown, MD, February 22, 1984. Invited
- Rains, T. C., "Atomic Absorption and Emission Spectrometry," ACS Short Course, IBM, Endicott, NJ, February 22-24, 1984.
- Barnes, I. L., "Trace Element Analysis - State of the Art," Southeastern Pennsylvania Section, American Chemical Society, Elizabethtown College, Elizabethtown, PA, February 23, 1984. Invited
- Kelly, W. R., "The Potential Use of Sulfur as a Tracer for Field Experiments," Working Group for the Atmospheric Field Experiment, Council on Environmental Quality, Washington, DC, February 29, 1984. Invited
- Norris, J. A. and Reed, W. P., "NBS Standard Reference Materials for the Metals Industries: Current Activities and Future Trends," Pittsburgh Conference, Atlantic City, NJ, March 1984.
- Moody, J. R., "Low Cost Alternatives in Clean Lab Design," Clinical Laboratory Seminar, Cleveland Clinic Foundation, Cleveland, OH, March 2, 1984. Invited
- Rains, T. C., "Atomic Absorption and Plasma Emission Spectrometry," ACS Short Course, Pittsburgh Conference, Atlantic City, NJ, March 2-4, 1984.
- Zhang, Z. K., "Determination of Germanium in Biological Fluids Using Electrothermal Atomization Atomic Absorption Spectrometry," Pittsburgh Conference, Atlantic City, NJ, March 8, 1984.
- Fleming, R. F., "Nuclear Depth Profiling--Applications in Material Science, Metallurgy and Semiconductor Devices," Departments of Nuclear Engineering and Materials Science seminar, University of Virginia, Charlottesville, VA, March 19, 1984.
- Kelly, W. R., "Use of Isotopes as Tracers for Atmospheric Environmental Problems," Inorganic Analytical Research Division Seminar, National Bureau of Standards, Gaithersburg, MD, March 20, 1984.
- Spielmann, K. S. and Blackman, M. J., "Trace Element Variability within an Outcrop: Smoky Hills Jasper from Collyer, Kansas," Second Conference on Prehistoric Chart Exploitation, Carbondale, IL, March 20, 1984.
- Deal, E. C., "Archaeometry, A New Approach to Old Problems - Determining the Provenance on Works of Art and Comparative Samples by Lead Isotopic Ratio Analysis," University of the District of Columbia, Chemistry Department, Washington, DC, March 21, 1984. Invited
- Fleming, R. F., "Neutron Depth Profiling at NBS," ONR Meeting on Chemical Instrumentation and Analysis, Midway, UT, March 24, 1984.
- Barnes, I. L., "Trace Element Analysis - State of the Art," Dallas-Ft. Worth Section, American Chemical Society, Southern Methodist University, Dallas, TX, March 26, 1984. Invited

- Barnes, I. L., "Trace Element Analysis - State of the Art," Heart o' Texas Section, American Chemical Society, Baylor University, Waco, TX, March 27, 1984. Invited
- Barnes, I. L., "Trace Element Analysis - State of the Art," Central Texas Section, American Chemical Society, Texas Air Control Board, Austin, TX, March 28, 1984. Invited
- Barnes, I. L., "Trace Element Analysis - State of the Art," San Antonio Section, American Chemical Society, University of Texas-San Antonio, San Antonio, TX, March 29, 1984. Invited
- Watters, R. L., Jr., "Progress in Instrumental Analysis: Developments in Atomic-Absorption, X-ray Fluorescence, and Plasma-Emission Spectrometry for the Analysis of Metals and Ores," Mintek 50 International Conference on Recent Advances in Mineral Science and Technology, Johannesburg, RSA, March 30, 1984. Invited
- Greenberg, R. R., Fleming, R. F., and Lindstrom, R. M., "Elemental Characterization of Four Coal Standard Reference Materials Via Instrumental Neutron Activation Analysis and Prompt Gamma-Ray Activation Analysis," Fifth International Conference on Nuclear Methods in Environmental and Energy Research, Mayaguez, PR, April 4, 1984.
- Rains, T. C., "Atomic Absorption Spectrometry," Elms College, Chicopee, MA, April 4, 1984. Invited
- Rains, T. C., "Sample Preparation - State of the Art," Elms College, Chicopee, MA, April 4, 1984. Invited
- Barnes, I. L. and Morales, P., "Understanding Stray Magnetic Fields," Inorganic Analytical Research Division Seminar, National Bureau of Standards, Gaithersburg, MD, April 5, 1984.
- Greenberg, R. R. and Carpenter, B. S., "High Accuracy/High Precision Determination of U-235 in Nondstructive Assay Standards by Gamma-Ray Spectrometry," Fifth International Conference on Nuclear Methods in Environmental and Energy Research, Mayaguez, PR, April 5, 1984.
- Watters, R. L., Jr., "Improving Accuracy in Atomic Spectrometry and Microanalysis," CSIR, Pretoria, RSA, April 5, 1984. Invited
- Zeisler, R. and Stone, S. F., "Evaluation of Biological Samples for Specimen Banking and Biomonitoring by Nuclear Methods," 5th Conference on Nuclear Methods in Environment and Energy Technology, Mayaguez, PR, April 6, 1984.
- Lindstrom, R. M., "Neutron Activation Analysis of Semiconductor Materials," ACS Meeting, St. Louis, MO, April 11, 1984. Invited.
- Downing, R. G., Maki, J. T., and Fleming R. F., "Application of Neutron Depth Profiling to Microelectronic Materials Processing," National ACS Meeting, St. Louis, MO, April 8, 1984. Invited

- Travis, J. C., Fassett, J. D. and Moore, L. J., "A Survey of Elements Detected Using RIMS with Thermal Vaporization," Second International Conference on Resonance Ionization Spectroscopy and Its Applications, Knoxville, TN, April 18, 1984.
- Koch, W. F., "Ion Chromatography," Society for Applied Spectroscopy Professional Development Program, Gaithersburg, MD, April 23, 1984. Invited
- Fassett, J. D., Travis, J. C., and Moore, L. J., "Thermal Atomization Sources And Resonance Ionization Mass Spectrometry (RIMS)," SPIE Symposium East '84, Arlington, VA, May 3, 1984. Invited
- Koch, W. F., "Review of Current Practices in the Measurement of pH in Acid Rain: Recommendations for the Future," Fourth Annual National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources, Raleigh, NC, May 10, 1984.
- Barnes, I. L., Brill, R. H., Deal, E. C., and Piercy, V. G., "Lead Isotope Studies of Some of the Finds from the Serce Liman Shipwreck," Symposium on Archaeometry, National Museum of Natural History, Smithsonian Institution, Washington, DC, May 14, 1984. Invited
- Deal, E. C., "Determining the Provenance on Works of Art and Comparative Samples by Lead Isotopic Ratio Analysis," International Archaeometry Symposium, Washington, DC, May 15, 1984. Invited
- Blackman, M. J., Olin, J. S., and Jornet, A., "The Use of Interlaboratory Data Sets in Provenience Studies," 1984 International Symposium on Archaeometry, Washington, DC, May 17, 1984.
- Jornet, A., Blackman, M. J., Westley, H., and Olin, J. S., "Study of Maiolica from Three Production Areas of Spain," 1984 International Symposium on Archaeometry, Washington, DC, May 17, 1984
- Olin, C. H., Cheng, Y., Blackman, M. J., and Olin, J. S., "Neutron Induced Autoradiography: A Novelty or a Useful Tool," American Institute of Conservation Annual Meeting, Los Angeles, CA, May 18, 1984.
- Rains, T. C., "State of the Art of Sample Preparation for Atomic Absorption and Emission Spectrometry," Rio Grande Section of Society for Applied Spectroscopy, Albuquerque, NM, May 18, 1984. Invited
- Kelly, W. R., "Application of Stable Isotope Tracers to Air Pollution Problems," Symposium on Simple Approaches to Complex Environmental Problems, ACS Middle Atlantic Regional Meeting, Newark, NJ, May 21, 1984. Invited
- Kelly, W. R. and Ondov, J. M., "The Use of Enriched Isotopes of Rare Earth Elements as Tracers of Aerosol," U.S.-DOE Workshop on Atmospheric Tracers, Sante Fe, NM, May 22, 1984. Invited
- Kelly, W. R., "The Use of Stable Sulfur Isotopes to Trace SO<sub>2</sub>," U.S.-DOE Workshop on Atmospheric Tracers, Sante Fe, NM, May 23, 1984. Invited

- Barnes, I. L., "Recent Advances in Mass Spectrometry," U.S. Geological Survey seminar, Reston, VA, May 25, 1984. Invited
- Cacic, C. G., Crawford, D. W., Machlan, L. A., "The Production and Provisional Certification of an Equal Atom Plutonium Isotopic Standard," 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, May 27-June 2, 1984.
- Powell, L. J., Fassett, J. D., and Moore, L. J., "Resonance Ionization Isotope Dilution Mass Spectrometry of Iron," American Society for Mass Spectrometry, San Antonio, TX, May 30, 1984.
- Diamondstone, B. I., "Standard Reference Materials - Their Importance for Transferring Technology," Department of Commerce Orientation Program, Washington, DC, June 19, 1984.
- Marinenko, G., "Proposed Electrochemical Primary Reference Methods for Ionized Calcium," American Association for Clinical Chemistry, Washington, DC, July 31, 1984.
- Norris, J. A., "Qualitative and Semi-Quantitative Emission Spectroscopy," Modern Industrial Spectroscopy Course, Arizona State University, Tempe, AZ, August 6-17, 1984.
- Rains, T. C., "Atomic Absorption and Plasma Emission Spectrometry," ACS Short Course, Metropolitan State College, Denver, CO, August 8-10, 1984.
- Zeisler, R., "An Analytical Approach to the Accurate Determination of Trace Substances in Biological Matrices," International Conference on Analytical Chemistry in Development, Colombo, Sri Lanka, August 24, 1984. Invited
- Travis, J. C., Turk, G. C., and Schenck, P. K., "Ultrasensitive Optogalvanic Spectroscopy," 1984 Annual American Chemical Society Meeting, Philadelphia, PA, August 28, 1984.
- Pratt, K. W. and Koch, W. F., "Determination of Trace-Level Cr(VI) in the Presence of Cr(III) and Fe(III) by Voltammetric Flow-Injection Analysis Without Prior Separation," 188th National Meeting of the American Chemical Society, Philadelphia, PA, August 29, 1984.
- Lindstrom, R. M., "Analytical Neutron-Capture Gamma-Ray Spectroscopy: Status and Prospects," 5th Intern. Symposium on Capture Gamma-Ray Spectroscopy and Related Topics, Knoxville, TN, September 10, 1984. Invited
- Travis, J. C., Turk, G. C., and Epstein, M. S., "Laser Induced Atomic Fluorescence in Flames with 5 kHz Pulsed Excitation," Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 16-21, 1984.

Beary, E. S., Paulsen, P. J., Lambert, G. M., "Determination of Selenium in Biological and Botanical Standard Reference Material's by SSMS Isotope Dilution," 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 17, 1984.

Zhang, Z. K., "Trace Determination of Antimony in Refractory Materials by Atomic Absorption Spectrometry," 11th Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Philadelphia, PA, September 18, 1984.

Greenberg, R. R., "Determination of Ultratrace Elements in Biological Materials by Neutron Activation Analysis," 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 19, 1984. Invited

Rains, T. C., "Sample Preparation Workshop," 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 19, 1984.

Moody, J. R. and Lindstrom, R. M., "The Selection of Apparatus and Containers for Trace Element Analysis of Biological Materials," 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 19, 1984.

Epstein, M. S., "Atomic Spectroscopy in the Certification of Reference Materials for Environmental Analysis," 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 20, 1984.

Turk, G. C., Watters, R. L., Jr., and DeVoe, J. R., "Resonant Laser-Induced Ionization of Atoms in an Inductively Coupled Plasma," 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 20, 1984.

Watters, R. L. Jr., and Zhang, Y. K., "The Effects of Various Solvents on ICP Analysis of Oils," 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 20, 1984.

Zeisler, R., "Analytical Procedures for the Accurate Determination of Trace Substances in Biological Media," XIX Yugoslav Meeting on Nuclear Medicine, Zadar, Yugoslavia, September 25-29, 1984. Invited

#### Committee Assignments

##### I. Lynus Barnes

Member, Department of Health, Education, and Welfare, The Chemistry Task Force of the National Shellfish Sanitation Program  
Washington Editorial Review Board  
International Union of Pure and Applied Chemistry, Commission of Atomic Weights and Isotopic Abundances

Chairman, IUPAC, Commission on Atomic Weights and Isotopic Abundances, Working Group on Statistics Applied to Atomic Weights



Robert W. Burke

Member, ASTM E-03, Chemical Analysis of Metals  
ASTM D-34, Standards for Waste Characterization

Barry I. Diamondstone

Member, ASTM D-34, Waste Disposal  
ASTM D-34.02.01, Section on Batch Extractions  
ASTM E-03, Chemical Analysis of Metals  
ASTM E-03.01, Gases in Metals  
ASTM E-03.93, Long Range Planning

Chairman, Task Force on Oxygen in Metals

Michael S. Epstein

Member, ASTM D-19, Water  
Editorial Advisory Board, Progress in Analytical Atomic  
Spectroscopy  
Treasurer, National Society for Applied Spectroscopy  
Chairman, Baltimore-Washington Section of the Society for Applied  
Spectroscopy  
Delegate, FACSS Governing Board for the Division of Analytical  
Chemistry of the American Chemical Society

Ronald F. Fleming

Member, ASTM E-10.05, Nuclear Radiation Metrology  
Organization Committee, Sixth Symposium on X- and Gamma-Ray  
Sources and Applications

John W. Gramlich

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

Robert R. Greenberg

Member, NBS Chemistry Storeroom Committee  
Trace Analysis Committee, Biomedical Division, American  
Nuclear Society

Howard M. Kingston

Member, ASTM C-26.05, Methods of Test  
ASTM C-26.07, Waste Materials  
Task Group Leader, C-26.05, Leachate Analysis Methods  
Congressional Science Fellow, Energy and Commerce Committee  
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

John K. Langland

Chairman, NBS Electronics Storeroom Committee

Richard M. Lindstrom

Alternate Member, NBSR Safety Evaluation Committee

Lawrence A. Machlan

Member, ASTM C-26, Nuclear Fuel Cycles  
ASTM C-26.05, Test Methods  
Secretary, ASTM C-26.01, Editorial and Terminology

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  
Councilor, National Capital Section of the Electrochemical Society

John R. Moody

Member, ASTM D-19, Water  
ASTM D-19.05, Inorganic Constituents in Water  
Audit Committee, Chemical Society of Washington  
Contamination Control Standards and Practices for Federal  
Standard 209c, Institute for Environmental Sciences  
Delegate, Society for Applied Spectroscopy  
Representative, FACSS Governing Board

Thomas J. Murphy

Member, American Chemical Society Committee on Analytical Reagents  
American Chemical Society Committee on Membership Affairs  
International Union of Pure and Applied Chemistry (IUPAC),  
Commission on Atomic Weights and Isotopic Abundances  
International Union of Pure and Applied Chemistry (IUPAC),  
Subcommittee for the Assessment of Isotopic Abundances  
Commission on Atomic Weights and Isotopic Abundances  
Chairman, American Chemical Society Admissions Committee  
Audit Committee, Chemical Society of Washington  
Councilor, Chemical Society of Washington

John A. Norris

Member, 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

Lura J. Powell

Member, Chemical Society of Washington  
Board of Directors, NBS Child Care Association  
Chairman, Committee on Isotope Ratio Measurements, American Society  
for Mass Spectrometry  
Treasurer, Chemical Society of Washington  
President, Standards Committee for Women

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-01, Paint and Related Coatings  
ASTM D-19, Water

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 (SIING) for project on "Atomic Absorption Spectroscopy"

Column Editor, Journal of Applied Spectroscopy

Ronald W. Shideler

Member, NBS Electronics Storeroom Committee

Yung-Chi Wu

Member, ASTM D-19, Water

Rolf L. Zeisler

Member, NBSR Safety Evaluation Committee

Chairman, Trace Element Analysis Committee, Technical Group for Biology and Medicine, American Nuclear Society

#### 4. Other

##### a. Seminars

November 8, 1983 - Mr. Richard J. Walker, Department of Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook, New York, "Petrogenesis of the Tin Mountain Pegmatites."

February 16, 1984 - Dr. Kenneth W. Pratt, Jr., Research Chemist, Electroanalytical Chemistry Group, Inorganic Analytical Research Division, National Bureau of Standards, Gaithersburg, MD, "Electrochemical Flow-Injection Analysis Using Vibrating Electrodes."

April 12, 1984 - Dr. Marcel De Bruin, Interuniversitair Reactor Instituut, The Netherlands, "Identification of Sources of Heavy Metal Air Pollution Using Multielement Analysis of Aerosol Samples and Biological Indicators: Possibilities and Limitations."

- May 3, 1984 - Dr. Judith R. Turnlund, Project Leader, Nutrients Research Units, United States Department of Agriculture, Berkeley, California, "Stable Isotopes of Trace Elements: New Tools for Human Nutrition Research."
- June 11, 1984 - Dr. Philip J. Savickas, Department of Chemistry, University of Virginia, "New Ionization Methods in Glow Discharge Mass Spectrometry."
- June 21, 1984 - Dr. Kenneth R. Thompson, Nuclear Data, Inc., Schaumburg, Illinois, "High-Speed Data Acquisition and Loss-Free Counting in Energy Spectroscopy."
- August 12, 1984 - Professor C. Th. J. Alkemade, University of Utrecht, Holland, "Distortions of Saturation Curves in Laser-Induced Atomic Fluorescence."

b. Conferences Sponsored

- November 11-16, 1984 - R. Zeisler, ANS-ENS International Conference: Special Sessions on Standardization of Collection and Preparation of Biomedical Samples for Trace Element Analysis, Washington, DC.

### III. Organic Analytical Research Division

Willie E. May, Chief  
Dennis J. Reeder, Deputy Chief

#### A. Division Overview

The Organic Analytical Research Division conducts research to develop and improve techniques for the preparation, purification, characterization, and analysis of organic compounds and uses these techniques in the solution of analytical problems related to national needs. The Division's research is carried out by five groups that are organized along functional lines: Bioanalytical Techniques, Electrochemistry, Gas Chromatography, Liquid Chromatography and Mass Spectrometry. As in the past, the Division has been actively engaged in the application of organic analytical chemistry to measurement problems related to energy, the environment, health and clinical chemistry, and food and nutrition. Results of the Division's research activities are utilized by industry, other Federal Agencies, public and private institutions and associations, and other research programs at the National Bureau of Standards. Research efforts during the past year have resulted in the publication of more than 50 articles in books and archival journals.

As in past years, our research efforts have primarily been in basic organic analytical chemistry, in support of other Federal agency requests and to a limited degree, in short-term projects performed on a service analysis basis. Substantial progress has been made in the chromatography program and in each of the Division's three Competence Building Programs; Organic Electrochemistry, Analyses of Ionization Mechanisms and Ion Structures in Organic Mass Spectrometry, and Bioanalytical Techniques - The Use of Proteins in Analytical Chemistry. Accomplishments in these areas will be discussed in the Group Overviews and Technical Reports that follow. As in the past, the major portion of our Other Agency support has come from the Environmental Protection Agency (EPA), the Department of Energy (DoE), and the Food and Drug Administration (FDA).

During the past year, our efforts included: providing three reference materials and analyses to establish NBS traceability on a number of calibration materials and proficiency testing samples to EPA; continuing to function as a reference laboratory for a network of DoE supported laboratories involved in the analysis of polar organics in energy related samples; critically evaluating methods used for the analysis of ethylene oxide on surgical tools for FDA; performing analyses in support of other NBS programs such as surveying the types and amounts of chlorinated compounds given off from the burning of refuse derived fuels, identifying daughter products of combustion that can be used as markers for the occurrence of arson, and service analyses performed for the Office of Standard Reference Materials, e.g., ethylene dibromide in wheat flour and stability of several SRM's previously certified.

We have continued our collaborative efforts with the Gas and Particulate Science and the Inorganic Analytical Research Divisions in the Bioanalytical Competence and Toxic Organics in Air Programs. Our collaboration with the Gas and Particulate Science Division has led to the development of an isotope dilution gas chromatography/mass spectrometric method for the

determination of toxic organic compounds in air at concentrations ranging from a few parts-per-billion (ppb) to 10 parts-per-million (ppm). This method will be used at NBS in the certification of multicomponent toxic organics in air standards. A sample transfer device developed as part of this program along with the appropriate gas standards will be used by EPA to determine compound specific detection limits and sensitivities for GC/MS systems. Additional details concerning this program are given in Technical Report 3, page 76. In our collaborative effort with the Inorganic Analytical Research Division, we have used neutron activation analyses to investigate metal/protein interactions and in elucidating the mechanisms responsible for protein visualization after silver staining (see Technical Report 7, page 80).

A considerable effort has continued to be devoted towards supporting the NBS Standard Reference Materials Program. Analytical measurements for the Certification of SRM 1614 (2,3,7,8-TCDD in Toluene), SRM 1643, (GC/MS Performance Evaluation Standard), SRM 1821A (Ethanol in Water) and Creatinine in SRM 909 (Human Serum), have been completed. We have initiated measurements on SRM's 41C (Dextrose), 1650 (Diesel Particulate Matter), and 1587 (Nitro-PAH in Methanol). This year a major effort was directed toward the development of methods to be used in the certification of future SRM's. Methods development began or continued on the determination of triglycerides in human serum, selected chlorinated pesticides and PCB's in cod-liver oil, dioxins in soils, and fat and water soluble vitamins in dry milk powder.

Our research programs in liquid chromatography and organic mass spectrometry were bolstered by the addition of a second NRC postdoctoral fellow in each of these areas. We were also successful in obtaining a postdoctoral research fellow for our Gas Chromatography Group. Dr. Kwokei Ng, a Research Associate supported by the College of American Pathologists left NBS in July, to accept a permanent industrial position. His replacement represents an immediate hiring priority. Dr's. Gary Byrd and Lane Sander will complete their two year postdoctoral terms October 1, 1984, but will remain with us in our Mass Spectrometry and Liquid Chromatography Groups, respectively. The acquisition of a biochemist with experience in enzyme immobilization techniques and procedures, and an electrochemist with expertise in the area of chemically modified electrodes continue to be of high priority.

In the coming year, we anticipate that our efforts will continue to be directed towards basic research to maintain and improve our measurement capabilities in each of our five groups (see Group Overviews for specifics), providing analytical support for problems of national importance, development of reference materials for specific sponsors, and certification of Standard Reference Materials. We expect to maintain support for our three Competence building programs and have requested support for another in "High Resolution Chromatography". We will expand our role as a National Reference Laboratory for trace organic chemical measurements to include a network of laboratories that are measuring blood serum levels of selected vitamins as part of the National Cancer Institute's Chemoprevention Program. We have been requested to develop "Drugs of Abuse in Urine" reference materials for use in the Department of Defense's Drug Screening Program and to develop confirmatory method for Chemical Warfare Agent BZ in blood and urine by the U. S. Army Medical Bioengineering Research and Development Laboratory. Finally, a joint proposal with the Center for Radiation Research, to identify unique compounds

resulting from food irradiation processing for possible use as chemical dosimeters, has been submitted to the Department of Health and Human Services.

## 1. Bioanalytical Techniques Group: Overview

The Bioanalytical Techniques Group has concentrated efforts in several areas that are broadly interrelated with research goals focused on (1) development of separation methods that are applicable to biotechnology, (2) high-accuracy determination of analytes of interest to the clinical community, and (3) maintenance of expertise and performance research in high-field nuclear magnetic resonance spectroscopy. These three areas of research reflect the directions that the group is taking. The biotechnology and spectrometry areas have been generally funded by the competence building program and the clinical work has been supported by STRS funding from the Office of Standard Reference Materials.

In work designed to further our understanding of biomolecule separations, we have continued to perform research in two-dimensional electrophoresis, thin-layer isoelectric focusing, and metal-ion affinity chromatography. Two-dimensional electrophoresis has been used to assess the usefulness of currently-available protein "markers" for molecular weight standardization and isoelectric focusing definition. While there are many available materials being used by laboratories to standardize electrophoretic systems, recent studies by our group have shown that marker proteins that are useful in one electrophoretic system may not be adequate for other systems. A critical evaluation of such standards has been an on-going project at NBS during the past year. Thin-layer isoelectric focusing (TLIEF) is being used as the prime analytical tool for identifying protein fractions from column chromatography experiments. In collaboration with several groups from the National Oceanographic and Atmospheric Administration (NOAA), we are using TLIEF to develop methods for the identification of several closely related fish species. We have also developed, in conjunction with a NOAA guest-worker, procedures for staining enzymes directly on thin-layer gels for assessment of genetic differences in squid species. Our work with metal-ion affinity chromatography has been extended to examine the behavior of selected enzymes on column supports to which various metals have been covalently bound. This work, directed toward understanding the role of the metal ion in binding proteins, should help in designing reagents, in developing purification techniques, and in producing new media for separating biomolecules.

Our work and interest in electrophoresis as a separation and identification technique led to our co-sponsoring with the Electrophoresis Society of the Americas, and hosting of a workshop in June, 1984 on "Electrophoresis Standardization: Approaches and Needs". The 54 attendees included leaders from various scientific sectors: fifteen industrial representatives; eight from universities; and the remainder from government agencies, including state crime laboratories, the National Aeronautical and Space Administration, National Institutes of Health, Uniformed Services University of the Health Sciences, and the Food and Drug Administration. Talks on various approaches to standardization in many areas of electrophoresis were presented. Because of the success of this workshop, NBS has been asked to address electrophoresis standardization issues at a national meeting of the

Electrophoresis Society and to coordinate an international interlaboratory comparison study involving the electrophoretic separation of a standard mixture of proteins.

Work has continued vigorously in organic analysis by NMR spectroscopy. Due to the complexity of the NMR spectra of biomolecules, there is a great need to exploit and develop methods that permit selective separation of NMR parameters and allow differentiation of structural types. For these reasons, we are extending our competence in the application of two-dimensional NMR methods to problems of bio-organic significance. We are also investigating the broader application of recently developed polarization transfer methods for NMR spectroscopy of liquids and of spectrum editing methods for structure elucidation. Improvements in NMR sensitivity are extremely important in trace organic analysis. Polarization transfer methods offer the possibility of such improvements for the NMR of heteronuclei via two major mechanisms: (1) signal:noise improvement proportional to the ratio of the magnetogyric constants of the proton and the heteronucleus being observed, and (2) dependence of the polarization transfer experiment relaxation properties on the relaxation times of the protons which are generally shorter than those of the heteronuclei. It is now believed that the efficiency, and hence the sensitivity and spectrum editing accuracy of polarization transfer experiments, is dependent on using short radiofrequency pulse widths for the excitation of samples. This can be a problem for the large sample tube sizes that are of prime interest for analysis of biological samples. Therefore, we are taking steps to upgrade the NMR pulse sequences to minimize the RF heating (and hence degradation) of polar solutions of biomolecules.

The NMR projects pursued this year include detection and measurement of the aldehydo forms of aldoses, measurement of the lactose content of the dried milk SRM 1549, investigation of the tautomerism of food dyes by  $^{15}\text{N}$  NMR, work on the structure of a growth hormone,  $^{13}\text{C}$  NMR of bovine serum albumin, two-dimensional J-resolved and proton-proton chemical shift correlated NMR of the angiotensin SRM 998, and complete assignment of the proton and  $^{13}\text{C}$  NMR spectra of four equilibrium anomers of digitoxose by two-dimensional proton-proton, and proton-carbon chemical shift correlation techniques, respectively.

Development of methods based on isotope dilution for the definitive quantification of analytes in human serum has continued in collaboration with the Mass Spectrometry Group. This past year, we concentrated efforts in refining the synthesis of labeled materials used in the ID/MS determination of creatinine. Work has also continued in the preparation of a labeled tripalmitin for use in the development of a triglyceride definitive method.

We have continued to perform analyses that are related to the Standard Reference Materials Program. This past year we have undertaken analyses leading to the characterization and certification of renewal SRM 41b, Dextrose. Extensive polarimetry studies have been made on this material. Homogeneity testing and structure confirmation have been performed by high-field proton NMR. The anomeric contents and purity of the dextrose were examined by both  $^{13}\text{C}$  and proton NMR since two independent analytical methods are required for SRM certified values.



Construction of the triple-module modernized laboratory for biotechnology is scheduled for the last quarter of FY84. This facility should relieve some of the congestion and improve efficiency in performing electrophoretic and chromatographic separations.

During the second year of the competence building program in the bioanalytical area, our staff size has remained stable, with the loss of several part-time personnel and the addition of a chemist who was retrained to perform electrophoretic separations. The search for a biochemist as an addition to the staff is still continuing. Several candidates have been interviewed and have given seminars. Two of the most promising prospects declined our offers and took other positions. There is intense competition with industrial biotechnology firms for highly qualified biochemists.

Under the guidance of Dr. P. V. Sundaram, Max Planck Institute for Experimental Medicine, Göttingen, Germany, we are beginning work on enzyme immobilization. During the last part of FY84, Dr. Sundaram will conduct a three-week hands-on workshop designed to transfer enzyme immobilization techniques to our staff. The ability to stabilize biomolecules by immobilization will assist us in developing new analytical reagents. This area of research is of prime importance in our development of procedures and standards for separation, identification and quantitation of biomolecules.

In FY85 we will continue to focus our efforts on improving our electrophoretic separation capabilities, applying neutron activation analysis to enhance our understanding of the mechanisms involved in protein staining and the nature of metal-protein interactions; and on defining the role of electrophoretic material purity on reproducibility of electrophoretic separations. In addition, we will continue our efforts in developing high-accuracy methods for analytes of importance in clinical chemistry, and in improving our NMR spectroscopy capabilities. We will expand our efforts in enzyme immobilization and develop techniques to examine glycoproteins and other large biomolecules. Research in the food/nutrition area will expand as coordination efforts with other laboratories involved in the National Cancer Institute Chemoprevention Program project is begun.

Dennis J. Reeder, Group Leader; Lyle A. Alexander, Alex Cohen, Bruce Coxon, Alexander J. Fatiadi, Diane K. Hancock, Cindy L. Hsu, Millard Maienthal, Kristy L. Richie, Robert Schaffer

## 2. Electrochemistry Group: Overview

A continuing need exists for the development of new approaches for trace organic and organometal analyses. Until recently, electrochemical techniques have not been widely used for such analyses because of their lack of resolution. The combination of chromatography with electrochemical detection and the advent of electrocatalysis at polymer-modified electrodes have provided new impetus for novel approaches in the analysis of organic compounds.

Our research efforts have continued to be focused on the study of organic and organometallic redox reactions using state-of-the-art electrochemical techniques: cyclic voltammetry, chronoamperometry, chronocoulometry, and rotating ring-disk electrochemistry; hybrid techniques, such as spectroelectrochemistry and liquid chromatography with electrochemical

detection; the preparation and evaluation of chemically modified electrodes; and mathematical modeling of electrochemical processes in support of the Group research activities.

In the organic electrochemistry competence building program we have continued to make good progress toward our research objectives and have applied these results to NBS programmatic needs. We have demonstrated the power and versatility of liquid chromatography with electrochemical detection (LCEC) for organometal speciation and biochemical analyses. Most successful to date has been the development of novel electrochemical detectors for chromatographic analysis. Multiple electrode designs and various excitation waveforms have resulted in significant advances in selectivity and sensitivity. In addition, we have pioneered the use of reductive electrochemistry which has greatly extended the applicability of this method of detection. For example, a new method was developed for the determination of nitro-PAHs using nonlinear gradient elution chromatography in combination with computer-controlled, potential-optimized, differential-pulse detection. Spectro-electrochemistry, both uv-visible and surface-enhanced Raman, has provided considerable useful information on reaction mechanisms and the molecular species adsorbed at the electrode surface. These studies have included the characterization of the electrochemical behavior of a series of transition metal dithio-oxocarbon complexes and the identification and fate of pyridine species at a silver electrode surface. The most promising area of research in terms of both understanding fundamental processes at electrode surfaces and providing a novel class of chemical sensors is that of the chemical modification of metal, semiconductor, and carbon electrodes. Problems associated with polymer-film stability and loss of activity of the electrocatalytic redox centers are being overcome and highly selective and sensitive analytical devices are expected to be feasible soon.

While the uv-visible transmittance approach will continue to be used to aid in the elucidation of redox mechanisms, Raman spectroscopy will be replaced by Fourier-transform infrared (FTIR) spectroscopy which provides similar in-situ capabilities but is not limited by electrode substrate material or analyte structure. This latter technique will allow us to probe interfacial and polymer-film phenomena which profoundly affect electrochemical behavior.

In the area of LCEC, our plans call for continued research to enhance the sensitivity of this technique by the development of microarray electrodes to increase the signal-to-noise ratio and the use of chemically modified electrode detectors to provide increased analyte specificity.

LCEC and polymer-modified electrocatalytic electrodes are potentially applicable to a diversity of analytical problems of considerable clinical, environmental, and military importance. Consequently, our goal is to extend the applicability of electrochemical sensors through a combination of fundamental research on the design of novel electrodes and on the electrode reaction mechanisms of organic analytes. Through this research, we expect to provide leadership in trace organic electroanalysis and a basic understanding of the electrochemical phenomena that can lead to state-of-the-art analytical methods and standards. Thus, the development of electrocatalytic sensors will be a major research thrust in the group because of their potential as novel analytical devices of high selectivity and sensitivity. Our mathematical models of the charge transport processes within the polymer films are

being refined and will provide new insights into optimal designs for this type of electrocatalytic sensor. The development of these sensors will not be limited to inorganic metal-complex catalysts but will be extended to enzymatic and immunological reactions via immobilized enzymes and antibodies confined to the electrode surface. The use of sensitive marker compounds encapsulated in synthetic biomembranes (liposomes and vesicles) which rupture when contacted by specific analytes, e.g., antigens or other types of biocomponents, also are feasible using electrode modification procedures. It is expected that biotechnological approaches will become more widely used based on their high reaction specificity and which, when combined with the sensitivity of electrochemical methods, will lead to unique classes of analytical sensors.

Our staffing level has remained stable and most of the major pieces of equipment acquired in past years are now operational. To expand our research efforts into the area of biotechnology, e.g., bioelectrochemical sensors, immunoelectrochemistry, etc., it would be desirable to increase our staffing to include a scientist knowledgeable in both biochemistry and electrochemistry. While the automation of selected instrumentation is progressing as planned, we are still in need of a versatile, rapid-scanning spectrophotometer and are collaborating with scientists at Ohio State University in the design and construction of a state-of-the-art instrument. In addition, we will require additional general purpose instrumentation, such as computer-controlled electrochemical systems, for the anticipated arrival of another graduate co-op student (R. Kannuck, Univ. of Md.) and a part-time guest worker (H. Blount, NSF). Also, new liquid chromatogenic equipment (pump, gradient mixer, data acquisition system, ADC, and computer software) is needed to maintain our competence in this area.

Richard A. Durst, Group Leader; Elmo A. Blubaugh, William A. MacCrehan, Gwendolyn S. Marbury, Scott R. Mund, Janet Sevy, William T. Yap

### 3. Gas Chromatography Group: Overview

The Gas Chromatography (GC) Group uses state-of-the-art chromatographic techniques to analyze for trace organic components of environmental, clinical, and consumer samples. The Group's goals are multifold. Primarily, we seek to maintain competence by updating our chromatographic capabilities through research in basic chromatographic science. An example of this is the effort to expand into the field's of multidimensional and supercritical fluid chromatographies. Secondly, the group seeks to promote trace organic Standard Reference Materials (SRM's) by proposing new SRM's and increasing the number of certified compounds in existing SRM's by additional chromatographic analysis.

We are undertaking a cooperative program dealing with the kinetics and recovery of PCDD in soils and marine sediments with scientists at the University of Maryland. Through this program, we hope to attain a working knowledge of how chlorinated compounds interact with environmental matrices and thus to design optimal procedures for their analysis. We are also engaged in a joint investigation with scientists in the Center for Material Science (CMS) on the feasibility of combining microspectrofluorimetric detection with capillary supercritical fluid chromatography (SFC). The detector developed in CMS, is capable of excitation beam focus at diameters of 50  $\mu\text{m}$  to yield an extremely high flux density which should be very

compatible with SFC and might be sensitive enough to detect polycyclic-aromatic hydrocarbons in normal gas chromatographic effluents. A spectro-fluorimetric detector may find considerable application in isomer specific analyses. The research into the identification of pollutant sources through gas chromatographic analysis of remotely collected air samples is approaching a successful conclusion. Two unique marker compounds, retene and levo-glucosane, have been identified and are being used for sample-source correlation.

During the past year we have expended major efforts in laboratory computerization and developing data handling algorithms (see Technical Report 11, page 83). Research directed towards SRM production was carried out on the determination of (1) polychlorinated biphenyls and pesticides in cod-liver oil, (2) 2,3,7,8-tetrachlorodibenzodioxin in soils, (3) polychlorinated biphenyls in human blood serum, (4) dinitro-pyrenes in a simple solvent matrix, and (5) polycyclicaromatic hydrocarbons in marine bivalves (freeze-dried mussels).

The GC Group has participated in a number of Other Agency funded projects. We worked with FDA on the determination of residual ethylene oxide in polymeric medical devices, with the Law Enforcement Standards Laboratory on the determination of arson accelerants, with EPA to establish traceability for their performance standards and to develop a PCB's in human serum reference material.

Research during the coming year will be concentrated in several distinct areas. First we shall study the thermodynamics and kinetics of the multiple-column separation process. Second, in order to be able to predict solute retention behavior, we will continue our studies on separations of complex congeneric mixtures with particular emphasis on the mechanisms of solute/matrix interactions and congeneric specific identification. Third, in support of the new National Cancer Institute chemoprevention program, we will investigate gas chromatographic methods for the analyses of vitamins A, C, and E.

The Group needs an additional four-channel, microprocessor-based integrator and a microcomputer for data management. A mass-selective GC detector is needed in the ultra-trace, isomer specific work, such as analysis of dioxins and furans in soils and polycyclicaromatic hydrocarbons in animal tissue.

The Group's personnel has had an overall increase due to the addition of one permanent staff member and one postdoctoral fellow. The two new members are Michelle M. Miller and Howard T. Mayfield. Ms. Miller is a Ph.D candidate at Georgetown University doing thesis research on the thermodynamics and kinetics of the chromatographic separation process. Dr. Mayfield is a NRC Post-Doctoral Fellow and will be investigating the basic aspects of multidimensional GC with particular emphasis on the theoretical prediction of solute retention. His work should lead to the ability to non-empirically choose the best combinations of gas chromatographic columns and temperature conditions for any separation of closely eluting solute pairs. Mr. Delmo P. Enagonio has retired this year, but is returning as a part-time, rehired annuitant. In addition to these staff changes, we have

two guest workers from the People's Republic of China who are spending a year with us to gain state-of-the-art proficiency in analytical capillary gas chromatography.

Stephen N. Chesler, Group Leader; Delmo D. Enagonio, Hui-Xiang Gu, Franklin R. Guenther, Hui-Cong Liu, Howard T. Mayfield, Michele M. Miller, Reenie M. Parris, Richard E. Rebbert

#### 4. Liquid Chromatography Group: Overview

The major activities of the Liquid Chromatography (LC) Group are directed towards (1) gaining a better understanding of the chemical and physical processes that contribute to retention and selectivity in LC and (2) applying this information to the development of methods for the isolation, separation, identification, and quantification of specific solutes in both simple and complex mixtures.

Research in understanding retention mechanisms has centered on the influence of both the stationary phase and the mobile phase on the retention process. Studies of stationary phase effects have continued to focus on the unusual properties of polymeric C<sub>18</sub> phases in comparison to the more conventional monomeric C<sub>18</sub> phases. Recent efforts in these studies have evaluated the influence of silica substrate characteristics on the column selectivity of the resulting bonded phase. Monomeric and polymeric C<sub>18</sub> bonded phases were prepared on 22 different silica substrates with pore diameters ranging from 50-1000 Å and the resulting bonded phases were characterized chemically (i.e., percent carbon) and chromatographically. Significant changes in selectivity, as well as absolute retention were observed as a function of pore size, with the greatest changes observed for the polymeric C<sub>18</sub> phases. The effect of silica pretreatment on the bonded phase synthesis and column selectivity was also examined. A model for the polymeric phase synthesis has been proposed where the extent of the reaction (i.e., degree of polymeric character) is limited by a size exclusion mechanism, hence the differences in behavior of phases prepared on different size pores.

These studies have provided an understanding of the essential factors required to produce C<sub>18</sub> phases capable of separating isomeric polycyclic aromatic hydrocarbons (PAH). An interesting separation on a polymeric C<sub>18</sub> column of 12 PAH isomers of molecular weight 278, with an elution order that correlates closely with the shape of the PAH solute, illustrates the high selectivity of these phases for resolution of such isomers. Future work in the study of stationary phase effects will attempt to characterize the unique features of the polymeric C<sub>18</sub> phase (e.g., physical topography and solute-stationary phase interactions) that produce this selectivity.

Research on the role of the mobile phase on selectivity in LC has been initiated by Dr. Joe P. Foley, a NBS/NRC Postdoctoral Fellow from the University of Florida. Dr. Foley has investigated the optimization of selectivity in isocratic reversed-phase LC via control of secondary chemical equilibrium (SCE). Computer simulations of data were used as guides in the derivation of new equations to predict the optimum conditions for the separation of specific solutes. These theories were then verified with the separation of monofunctional acids and bases on C<sub>18</sub> columns using pH buffered aqueous mobile phases. In the coming year, this approach will be used to expand the investigation from isocratic to gradient elution systems.

In the area of supercritical fluid chromatography (SFC), an instrument for use in SFC with a carbon dioxide mobile phase on packed LC columns was obtained and made operational. Preliminary evaluations of the analytical capabilities and uses are currently in progress. Investigations of the retention mechanisms of SFC, in particular as compared to conventional LC, are planned for the coming year. The potential of SFC for accurate quantitative analysis will be evaluated and compared to more conventional chromatographic techniques.

During the past year, LC methods have been developed and are being applied to the certification of two environmentally significant SRM's: SRM 1650 "Diesel Particulate Matter" and SRM 1587 "Nitrated Polycyclic Aromatic Hydrocarbons in Solvent". For the analysis of the diesel particulate matter, normal-phase LC is used to isolate the PAH into two fractions (PAH with 16 or less aromatic carbon atoms and those with 18 to 24 aromatic carbon atoms). A total of 12 PAH will be determined in these two fractions by using reversed-phase LC with fluorescence detection. SRM 1587 "Nitrated Polycyclic Aromatic Hydrocarbons in Solvent" will consist of several mixtures of mono- and dinitro-PAH. The LC methods developed will separate the specific nitro-PAH in the SRM (i.e., six mononitro-PAH and three dinitropyrenes).

The LC Group continues to be involved in the measurement of environmentally important substances. Multidimensional LC/LC and LC/GC approaches were used in the analysis of a coal tar sample to identify and quantify the PAH in this complex matrix. A series of performance evaluation samples, prepared for EPA by an outside contractor, was analyzed using LC with two different detection methods (uv-absorption and post-column derivatization with fluorescence) as part of their quality assurance process. Reversed-phase and normal-phase retention data for about 70 polychlorinated biphenyl (PCB) congeners have been obtained as part of an effort to evaluate the feasibility of using LC, in addition to GC, to quantify PCB's in the proposed cod-liver oil SRM.

In conjunction with the Mass Spectrometry Group, research in the use of mass spectrometry (MS) as an LC detector has continued. In the past, LC-MS has been used to quantify individual organic compounds in complex mixtures (e.g., phenol and cresols in shale oil). However, interferences frequently occurred. The additional selectivity of a triple quadrupole MS with collisionally activated dissociation has been used to overcome this problem. Using this approach, dibenzothiophene was determined in a coal liquid and a crude oil sample. The analysis required no sample pretreatment and had a detection limit of 20 ng. In fact, the selectivity of MS-MS almost renders the LC separation unnecessary. Future work will center on analytical applications to exploit the potential of LC-MS-MS.

Two guest workers in the LC group have been involved in studies related to environmental measurements. Dr. Jan T. Andersson, a guest worker from the University of Ulm, Federal Republic of Germany, is investigating the use of LC to separate polycyclic aromatic sulfones [produced as the oxidation products of polycyclic aromatic sulfur heterocycles (PASH)] as part of a project to isolate and measure PASH in environmental samples. Dr. Azza Aziz Moustafa, from the Cairo University in Egypt and sponsored by an AMIDEAST Peace Fellowship, joined the LC group in September and is involved in the measurement of pollutants in environmental samples.

Future efforts related to the analysis of environmental samples will involve the determination of more "polar" compounds (e.g., hydroxyl-, nitro-, and, cyano-substituted polycyclic aromatic compounds and polycyclic aromatic ketones and quinones). These types of compounds (often containing more than one polar functionality) have been tentatively identified in air and diesel particulate samples in the "moderately polar and polar" fractions (generally isolated by classical column chromatography) which have been found to have significant mutagenic activity. However, the determination of these compounds presents a formidable task since they are relatively non-volatile and few authentic standards are available. LC offers the greatest potential for isolation and separation of these compound types.

In the area of food and nutrition measurements, work has continued in LC methods development for selected water- and fat-soluble vitamins in a non-fat dry milk powder (SRM 1549) and an infant formula material. Concentration values for ascorbic acid were obtained for SRM 1549; however, levels of the fat-soluble vitamins of interest in this sample were relatively low. As a result, an infant formula matrix, which contains higher levels of vitamins D<sub>2</sub> and A, has been used in the development of methods for the determination of fat-soluble vitamins in a milk matrix. An LC method was also used for the determination of lactose in SRM 1549 and results compared favorably with those obtained by NMR.

LC methods were developed and employed for the measurement of solutes of clinical and nutritional significance. The three isomeric forms of bilirubin (denoted 9 $\alpha$ , 3 $\alpha$ , and 13 $\alpha$ ) are all present in SRM 916 "Bilirubin"; however, this material is certified only for total bilirubin. These isomers are readily separated by LC, but quantitation by uv detection is difficult since each isomer has a different uv molar absorptivity. The molar absorptivity of each isomer was determined and this information was used to calculate the isomeric content of SRM 916. With the initiation of a new program to provide quality assurance standards for the National Cancer Institute in the measurement of selected vitamins in human serum, our efforts in the nutrition area will expand in the coming year. As part of this program LC methods will be developed and evaluated for the measurement of vitamin C (ascorbic acid), vitamin A (retinol), vitamin E ( $\alpha$ -tocopherol), and  $\alpha$ - and  $\beta$ -carotene in human serum.

Stephen A. Wise, Group Leader; Jan T. Andersson, Bruce A. Benner, Jeanice M. Brown-Thomas, Nicole C. Chessick, Richard G. Christensen, Joe P. Foley, Walter F. Kline, Sam A. Margolis, Azza A. M. Moustafa, Lane C. Sander, John P. Sullivan, and Karen D. Timmons.

## 5. Mass Spectrometry Group: Overview

The Mass Spectrometry Group has undertaken research in several areas involving both basic and applied research. The major continuing efforts have been directed to the development of mass spectrometric methods for the accurate quantification of individual compounds in complex mixtures, the development of an isotope dilution method for hazardous chemicals in gases at the ppb level, and to the laser induced photodissociation of ions and the collision induced dissociation of ions as part of the competence building

program in mass spectrometry, "Analysis of Ionization Mechanisms and Ion Structures". A number of the specific results of these efforts are included in the Technical Reports Section.

The quantitative measurements made are concentrated in the environmental and clinical areas. Measurements of chemical compounds in environmentally important materials have generally been of small molecules at low levels (ppm to ppb) for the purpose of providing SRM's or reference materials for other agencies. High-resolution capillary column gas chromatography/mass spectrometry with selected ion monitoring has provided the selectivity and sensitivity necessary for quantification of individual organic compound species in these complex samples. The need for specific measurements has been one of the driving forces behind an ongoing investigation of negative ion chemical ionization mass spectrometry. The initial results of these investigations were reported last year. Those results plus recent findings will appear in Analytical Chemistry, and are summarized in Technical Report 2, page 75.

We plan to continue the ongoing studies with which the group is involved with special attention to further investigation of the underlying mechanisms and utility of negative ion chemical ionization.

As part of a joint project with the Gas and Particulate Science Division for the EPA on research leading to standards for hazardous chemicals, the Mass Spectrometry and Gas Chromatography groups are developing a method for measuring toxic organic compounds in gases at the ppb to ppm level. The results are summarized in Technical Report 3, Page 76. The method will provide EPA with a direct way to determine the sensitivity of a GC/MS system and NBS with an independent method for certifying the concentrations of organic compounds present at low levels in gases.

The clinically related efforts, conducted in collaboration with the Bioanalytical Techniques Group, have centered on the development of definitive methods based on isotope dilution and gas chromatography for the quantification of human serum constituents. A Human Serum Standard Reference Material, SRM 909, was released in 1980 and now has values certified for the organic analytes cholesterol, glucose, uric acid, urea, and creatinine. The methodology developed for determination of urea has recently been published in Analytical Chemistry and that for creatinine appears in Technical Report 1, page 74 with publication planned for the latter part of this year. The methods developed for the certification and stability testing of the Human Serum SRM have also been used to place values on analytes in serum pools supplied by the Centers for Disease Control and in the serum pools distributed by the College of American Pathologists in their extensive laboratory surveys. During the coming year, we intend to develop a definitive method for triglycerides and provide a certified value for SRM 909.

The competence building program in mass spectrometry, "Analysis of Ionization Mechanisms and Ion Structures", was begun in October 1980. Two of the several activities included are in the Mass Spectrometry group. One of these involves laser induced metastable ion generation as a selective probe for molecular structure. The wavelength dependent photodissociation of ions created by electron impact was observed for a variety of molecules and this year one of the major milestones of the program, the observation of the photodissociation of ions generated by soft ionization techniques, was



achieved. The results are presented in Technical Report 4, page 76. One of the significant disadvantages of the soft ionization techniques is the lack of molecular structure information available. During the next year, we will investigate the photodissociation of ions generated using a cesium ion gun to see if photodissociation can be used to obtain that information.

We have been fortunate to have Dr. Kwokei Ng with us for the past year as the Roger K. Gilbert/College of America Pathologists Fellow. Dr. Ng has been responsible for the mass spectrometry part of the definitive methods measurements. We are pleased to have Mrs. H. X. Gu and Mr. Y. Gao from the People's Republic of China involved in the activities of the Group.

Edward White V, Group Leader; Gary D. Byrd, Laurence R. Hilpert, Yuji Gao, H. X. Gu, Stanley Meiselman, Daniel J. Pereles, Lorna T. Sniegowski, Michael J. Welch, Timothy J. Wozniak

B. Selected Technical Papers  
(Organic Analytical Research Division)

1. Development of a Definitive Method for Serum Creatinine (15320)

A. Cohen, K. Ng, R. Schaffer, M. J. Welch, and E. White V

The measurement of serum creatinine levels is an important and frequently used test for renal function. As part of an on-going program to develop definitive methods for organic analytes in serum, we have developed an accurate and precise isotope dilution mass spectrometric method for serum creatinine. We have used this method to certify the concentration of creatinine in SRM 909, a freeze-dried human serum, and to assign definitive values to serum pools used in a round-robin evaluation of a reference method and to College of American Pathologists Survey sera.

Briefly, the method consists of addition of a known weight of creatinine- $^{13}\text{C}_2$  (synthesized at NBS) to a known weight of serum. After an overnight equilibration, the serum is put on a weak acid resin column to separate creatinine from creatine. The creatinine is then derivatized with 2,4-pentanedione, acetic acid, and ethanol to form the ethyl ester of N-(4,6-dimethyl-2-pyrimidinyl)-N-methylglycine.

Samples are introduced into a low resolution, magnetic sector mass spectrometer via a gas chromatograph equipped with a non-polar glass capillary column. The magnetic field is switched between  $m/z$  150 and 152, the most abundant electron impact fragment ions for the unlabeled and labeled forms of the creatinine derivative, respectively. The intensities measured at each mass are summed separately across the GC peak and the sums are ratioed. For calibration, standards consisting of known amounts of unlabeled and labeled creatinine derivatives are measured immediately before and after each sample and are chosen such that their ratios bracket that of the sample. Each sample is remeasured on a separate day with the order of standards reversed.

With proper care at each step, this method yields results of high precision. For example, for the measurements of SRM 909, three sets consisting of six samples each were measured and found to have a relative standard deviation of 0.18% for a single measurement. To prove accuracy is more difficult, but it is possible to demonstrate an absence of bias in the measurement process. To do this we remeasured eight samples from the three sets by two other methods: (1) using ammonia chemical ionization for generation of  $(M+1)^+$  ions for measurement; and (2) using a fused silica column and another ion source for measurement of  $M^+$  ions. The three different measurements gave mean results for the eight samples which differed by less than 0.06%.

Manuscripts are in progress for definitive methods for creatinine and uric acid. A paper describing the definitive method for serum urea appeared in Analytical Chemistry, Vol. 56, pages 713-19, 1984, following earlier publications for cholesterol and glucose definitive methods. Work is now in progress on a definitive method for serum triglycerides.

2. Investigation of Factors Affecting the Selectivity of Negative Ion Chemical Ionization Mass Spectrometry for Isomeric Polynuclear Aromatic Hydrocarbons (26108)

G. D. Byrd and L. R. Hilpert

Negative ion chemical ionization mass spectrometry has been shown to give excellent selectivity for the detection of certain compounds in specific classes of organic compounds, and high sensitivities for those compounds in complex materials. We have observed the molecular anion of benzo(a)pyrene (BaP) to be more than 1000 times more abundant than that of its isomer benzo(e)pyrene (BeP) under certain ion source conditions using electron capture negative ion chemical ionization [1]. During the past year we have studied the pressure and temperature dependence of the selectivity for detection of BaP. The variation in the selectivity for detection of BaP to BeP was measured as a function of ion source pressure over a range of source pressures from 0.1 to 1.2 Torr (13.3 to 160 Pascal). The selectivity of detection, defined as:

$$\frac{(\text{Abundance of BaP molecular anion/ng BaP})}{(\text{Abundance of BeP molecular anion/ng BeP})}$$

decreased by an order of magnitude in going from low to high pressure.

The absolute sensitivity for the detection of BaP was also measured as a function of the ion source pressure. The absolute sensitivity for a species depends, in part, on the extent to which the newly formed and excited molecular anions can be stabilized by interactions with reagent gas molecules through the process of collisional stabilization. Collisions can also lead to fragmentations, however, with a resulting decrease in the molecular anion abundance and thus a decrease in sensitivity. The BaP signal ( $m/z$  252) was a maximum at a pressure of  $3.0 \times 10^{-4}$  Torr (0.04 Pascal) in the ion source manifold and 0.45 Torr (60 Pascal), in the source.

The variation in the selectivity of detection for BaP to BeP was also measured as a function of the ion source temperature over a range of source temperatures from 100 to 250 °C at a constant source pressure. As the source temperature was increased from 100 to 200 °C, the abundance of the BaP molecular anion increased relative to that for BeP, and the optimum selectivity was observed at 200 °C. The absolute sensitivity for the detection of BaP was also monitored as a function of source temperature and was a maximum at approximately 150 °C.

The reasons for the increased production of BaP molecular anion over that of BeP are still unclear and must await the results of additional experiments. However, the analytical capability of negative ion chemical ionization mass spectrometry is enhanced by our ability to change both the selectivity of detection for BaP and the absolute sensitivity for detection of BaP by carefully adjusting the ion source pressure and temperature.

[1] Hilpert, L. R., Byrd, G. D., and Vogt, C. R. Selectivity of Negative Ion Chemical Ionization Mass Spectrometry for Benzo[a]pyrene, *Anal. Chem.* 56 (11), 1842, 1984.

3. Development of an Isotope Dilution GC/MS Procedure for Analysis of Toxic Organics in Air Mixtures (15320)

G. D. Byrd, S. N. Chesler, R. G. Christensen, L. T. Sniegowski, and E. White V

As part of an EPA project for the analysis of trace toxic organic compounds in air, a method for cold-trapping of organic compounds at ppb levels was developed. Analysis is by gas chromatography/mass spectrometry (GC/MS) with labeled compounds used as internal standards. The method serves two purposes; a sensitivity check of a GC/MS system as a whole using an SRM, and as a second method for certification of trace level organics in gas cylinder SRM's. This method will be used for the analysis of toxic organic compounds in air for EPA, and for the analysis of organic compounds in compressed gases, such as nitrogen, for certification of SRM's.

The trap developed consists of a coil of stainless steel tubing and has a low dead volume. A valve placed between the gas cylinder and the trap controls the flow of gas through the trap, and a heated injection port on the trap allows introduction of liquid samples for spiking. The coil is cooled in dry ice-ethanol for trapping of organic compounds, which are later desorbed by electrical heating. The desorbed material is injected onto the GC column through a needle at the end of the coil.

Cylinders of bromobenzene in nitrogen at levels of 25 ppb and 1 ppb have been analyzed using this trap. The method consists of flushing bromobenzene through the warm trap and then trapping the bromobenzene by cooling the trap in a bath of dry ice-ethanol while measuring the volume of gas passed through the trap with a wet test meter. A spiking solution of bromobenzene- $d_5$  is added through the heated injection port, the mixture of labeled and unlabeled compounds is desorbed into the GC/MS, and the ratios of labeled to unlabeled bromobenzene are measured. A cylinder previously determined to be  $25.3 \pm 2.5$  ppb by GC and gravimetric preparation in the Inorganic Analytical Research Division was measured at  $26.0 \pm 2.0$  ppb using the GC/MS trapping method. Similarly, a cylinder determined as  $1.3 \pm 0.2$  ppb was measured at  $1.53 \pm 0.15$  ppb with our method. In both instances the error bars overlap for the two values.

Now that the trapping method has been demonstrated to work satisfactorily with bromobenzene, a four-component mixture of benzene, toluene, chlorobenzene, and bromobenzene in nitrogen at the 10 and 0.25 ppm levels will be analyzed by the same method.

4. Photodissociation of Ions Generated by Soft Ionization Techniques (26108)

D. J. Pereles, R. L. Sams, J. C. Travis, M. J. Welch, and E. White V

The soft ionization techniques, field ionization (FI), field desorption (FD), and fast atom bombardment (FAB), are widely used to characterize fragile molecules. Important structural information is often missing, however, since little or no fragmentation is observed with the first two techniques and the limited fragmentation observed with fast atom bombardment is often obscured by other processes. To obtain this structural information, energy must be added to the ion to induce fragmentation. This increase in

the internal energy of the ion can be accomplished by colliding the ion with a neutral molecule or by absorption of one or more photons. Collision induced dissociation has been widely used as a tool for structure determination, but photodissociation has not, although it is potentially more selective since the energy can be more precisely controlled. The photodissociation of ions has therefore been investigated as part of the mass spectrometry competence building program to see if the technique might be useful for obtaining structural information on molecules whose mass spectrometry requires the use of soft ionization techniques.

A Mattauch-Herzog geometry mass spectrometer has been modified to permit irradiation of ions in the first field-free region by light from an argon ion laser, and the ions formed in the field-free region have been studied using both accelerating voltage scans and linked magnetic field electric sector voltage (B/E) scans.

The fragmentation of n-butylbenzene has been studied by a variety of techniques and we have examined the photodissociation of n-butylbenzene generated by electron impact for comparison with earlier published results. Our results for m/z 91/92 ratios versus photon energy ranged from 0.4 to 2.0 which is substantially lower than the previous results where ratios increased from 1 to 7 over the same photon energy range. Our results were reproducible, and independent of both the type of scan (B/E or accelerating voltage) and laser beam path. They are in reasonable agreement with results from charge exchange mass spectrometry measurements. The magnitude of the difference in the results of the two photodissociation studies is not understood. We have also examined the effect of a high power pulsed laser and observed a strong dependence of the m/z 91/92 ratio on power, an effect not observed with the argon ion laser and not predicted by the published model. Although small molecules are not our main interest, we intend to pursue the matter by investigating a more comprehensive model of the processes occurring.

The particular experimental arrangement which we have constructed has allowed us to demonstrate for the first time the photodissociation of ions generated by soft ionization techniques, specifically field ionization and field desorption. The photo-induced metastable transitions observed for field ionized species include: for n-butylbenzene, m/z 134+92 and 134+91; for nitrobenzene, 123+77; and for 3,5-dinitrobenzoic acid, 212+166. This last metastable transition was not observed in the absence of laser light. The photo-induced metastable transitions observed for field desorbed species include: for cresol-red, m/z 382+302; for Sudan IV, 380+223; and for methyl red, 269+148. All of these transitions were also observed without laser light, but were enhanced by up to 60 percent with laser light. The magnitude of the methyl red transition was wavelength dependent. The parent ion in all cases where photodissociation was observed was M<sup>+</sup>.

Plans for the immediate future include: installation of a cesium ion gun to provide a more intense and stable ion beam and to allow investigation of the photodissociation of the larger molecules to which FAB provides access; improvements in the laser beam-ion beam interaction; and modifications of the data system required to allow the acquisition and signal averaging of data from metastable scans. If the planned experiments demonstrate convincingly the potential of the photodissociation of ions as a

technique for the determination of the structure of large organic molecules as expected, a choice will be made among the several, very different approaches to an analytically useful instrument.

5. Investigation of Ion/Molecule Reactions in a Triple Quadrupole Mass Spectrometer (26108)

R. G. Christensen, E. White V, and T. J. Wozniak

Tandem mass spectrometers, and in particular triple quadrupole mass spectrometers, are becoming more widely available in analytical laboratories. The most common use of the MS/MS technique is to look at collision-induced dissociation of ions, a process in which ions selected by the first mass analyzer collide with target gas molecules while passing through the center quadrupole, and the resulting fragment ions are scanned by the final quadrupole. The advantage over more conventional mass spectrometers is the added selectivity made possible by the addition of a second mass analysis step. The collision process also has the potential for considerable selectivity if the collision gas is chosen to allow for more chemistry than simple dissociation in the ion-molecule reaction occurring in the center quadrupole. Therefore, it was decided to investigate the selectivity of formation of adduct ions.

Since it is generally not possible to discriminate between isomers of polynuclear aromatic hydrocarbons by collision-induced dissociation, discrimination by adduct formation, if found, might be analytically useful.

A series of 3-, 4-, and 5-ring PAH were tested, including several isomer pairs. They were allowed to react at low collision energies with various reagent gases, including hydrocarbons, water, nitrogen, and various amines. Because of the design of the ion source, the ions have a range of collision energies of approximately 0-3 V. For initial investigations, this is thought to be an advantage, providing a wider range of conditions for adduct formation.

Comparing the ion current for the parent with that for the adducts [M+A yielding (M+A)<sup>+</sup>, (M+A-1)<sup>+</sup>, etc.] showed relative adduct formation ranging from several parts per thousand for some PAH, and up to sixty percent, in the case of a fluorene-pyridine adduct. Differences between some isomers were observed with some gases, but not with others. For example, water gives about a 5-fold difference in adduct formation with anthracene and phenanthrene, as does ammonia between benzo(a)pyrene and benzo(e)pyrene. It was noted that pyridine forms adducts very strongly with the PAH containing 5-membered rings.

Other areas to be investigated are the use of reactive target gases such as acetylenes, and trials with compounds having heteroatoms, such as nitrogen-containing heterocyclic PAH.

6. Analysis of the Proton and Carbon-13 NMR Spectra of Equilibrated Digitoxose by Two-Dimensional, Chemical Shift Correlation Methods (15320)

B. Coxon

In a previous report [1], we described the development of a new radio-frequency pulse sequence for performing two-dimensional (2D) heteronuclear J-resolved NMR spectroscopy with sensitivity enhancement by the DEPT (Distortionless Enhancement by Polarization Transfer) method. A key feature of this method is the ability to distinguish carbon-hydrogen groups of differing multiplicities. For this reason, digitoxose (the carbohydrate component of the cardiac glycosides digoxin and digitoxin) was selected as a model for demonstration of the method, since this sugar contains all three types of carbon-hydrogen groups, namely CH, CH<sub>2</sub>, and CH<sub>3</sub>. During the course of this work, we discovered that solutions of the single anomer β-D-digitoxopyranose in dimethylsulfoxide-d<sub>6</sub> equilibrate quite rapidly (2-3 days) to give a mixture of five forms that have now been characterized and identified by <sup>1</sup>H and <sup>13</sup>C NMR techniques as being two pyranoses, two furanoses, and an open-chain aldehydo form.

Application of the 2D DEPT heteronuclear J-resolved <sup>13</sup>C NMR technique to the equilibrated mixture yielded the gross assignments for the CH, CH<sub>2</sub>, and CH<sub>3</sub> structural types for the four ring forms only because, at a concentration of 0.1%, the aldehydo form is beyond the dynamic range of the 2D NMR methods used. The problem of assigning the complex methine carbon region completely has been tackled by using a combination of 2D <sup>1</sup>H→<sup>1</sup>H and <sup>13</sup>C→<sup>1</sup>H chemical shift correlation methods. Complete <sup>1</sup>H NMR assignments for the equilibrated mixture were first generated by application of 2D <sup>1</sup>H→<sup>1</sup>H chemical shift correlation, a technique that yields a 2D spectrum with <sup>1</sup>H chemical shifts in both dimensions. The observation of off-diagonal "cross peaks" indicates which protons are spin coupled to each other, and a spin coupling connectivity pathway was traced through the 2D spectrum for each ring form in turn. Assignment of the complex <sup>1</sup>H NMR spectrum of the mixture by conventional spin decoupling techniques would have required 40 separate experiments. In this way, a complete set of <sup>1</sup>H chemical shifts and almost complete sets of CH and OH <sup>1</sup>H→<sup>1</sup>H coupling constants were measured for the four ring forms of digitoxose. Although digitoxose is a structural homolog of 2-deoxy-D-ribose, the <sup>1</sup>H→<sup>1</sup>H coupling constants of the pyranoid forms of digitoxose indicate that they exist in chair conformations different from those of 2-deoxy-D-ribose [2]. This difference is attributed to the conformational locking effect of the methyl substituent in digitoxose.

With the <sup>1</sup>H NMR assignments in hand, detailed <sup>13</sup>C NMR assignments were then made by 2D heteronuclear <sup>13</sup>C→<sup>1</sup>H chemical shift correlation, a process that is mediated by the one-bond <sup>13</sup>C→<sup>1</sup>H coupling constants. For this work, a new technique [3] was used that gives <sup>1</sup>H decoupling in both the <sup>1</sup>H and <sup>13</sup>C dimensions. This method collapses most of the <sup>1</sup>H→<sup>1</sup>H multiplets in the 2D <sup>13</sup>C→<sup>1</sup>H chemical shift correlated <sup>13</sup>C NMR spectrum, thus leading to sharper peaks and increased sensitivity. For the four ring forms of digitoxose, all of the vicinal <sup>1</sup>H→<sup>1</sup>H coupling constants were removed by this technique. However, for the α-pyranose, β-pyranose, and α-furanose forms that have non-equivalent protons at C-2, the geminal couplings ( $J_{2,2'}$  ~ 14 Hz) between these protons remained in the 2D <sup>13</sup>C→<sup>1</sup>H correlated spectra, thus affording a

further useful selectivity. The H-2 and H-2' protons of the  $\beta$ -furanose form are chemically equivalent and hence their geminal coupling constant did not appear in the 2D  $^{13}\text{C} \rightarrow ^1\text{H}$  correlated spectra.

The complete set of  $^{13}\text{C}$  chemical shift assignments obtained for the four ring forms of digitoxose allowed the dependence of the shifts on ring size to be ascertained. The four ring forms were also measured quantitatively by both  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and good agreement between the two methods was observed.

[1] B. Coxon, in Technical Activities 1983, Center for Analytical Chemistry, H. S. Hertz, R. A. Velapoldi, and J. K. Taylor, Eds., NBSIR 83-2786, p. 149; see also B. Coxon, Abstracts 24th Experimental NMR Conference, Asilomar, CA, April 10-14, 1983.

[2] B. Coxon, J. Carbohydr. Chem., special NMR issue, in press.

[3] A. Bax, J. Magn. Reson., 53, 517 (1983).

7. Identification of Metal Binding Proteins in Polyacrylamide Gels by Neutron Activation Studies (26111)

D. Hancock, D. Reeder, S. Stone, and R. Zeisler

Over the past two years, we have developed techniques for the separation of complex protein mixtures using two-dimensional gel electrophoresis. The samples are separated into polypeptide maps which consist of several hundred protein "spots" in a polyacrylamide matrix. The protein spots are generally detected using non-specific protein stains such as Coomassie Blue or the more sensitive silver stain.

Identification of the individual spots remains a difficult problem. One approach to this problem is to apply a detection method that is more discriminating than the general protein stains. Recently, we have begun to apply neutron activation analysis techniques to polyacrylamide gels to determine the feasibility of detecting specific metal-binding proteins as well as phosphoproteins. Our results show that two-dimensional electrophoresis gels can be prepared with a low background of metals, a prerequisite for trace analyses. Metal-binding proteins such as carbonic anhydrase (which usually binds zinc) are easily detectable although it appears that some proteins may act as metal scavengers, accumulating an array of trace metals.

Neutron activation analysis is also being used on silver-stained gels to gain mechanistic information on this widely-used, but rather ill-defined and troublesome staining technique. This information will be used to establish staining conditions on a more scientific basis than the empirical approach presently used.

Future research with neutron activation techniques will address the interrelationships between trace elements and biological macromolecules during bioanalytical separations. Knowledge of the mechanisms of interactions may be gained by studying the in vitro and in vivo functions of the trace elements in the macromolecules. These investigations may provide new tools for the specific qualitative and quantitative determinations of these molecules in complex natural protein mixtures.



8. Squid Species Differentiated by Use of Thin Layer Isoelectric Focusing  
(26111)

C. L. Hsu, D. J. Reeder, and K. L. Richie

During the past year, NBS has been involved in a collaborative effort with scientists at the National Oceanic and Atmospheric Administration (NOAA) in an attempt to differentiate squid species using thin layer isoelectric focusing (TLIEF). The market for squid is increasing in commercial importance and is rapidly becoming a growing area of export. Thus arises the need by NOAA to assign a total allowable catch for squid so that export quota can be determined. However, to prevent overfishing of particular species of squid, the different species must be identified. This problem is best approached by using TLIEF which involves the separation of proteins in an electric field due to differences in their charge.

Squid were collected from the Pacific Ocean within a 1000 mile radius of Midway Islands by a NOAA researcher. The squid were subsequently classified according to their weight, length, and location when caught. Samples were stored at -60 °C until analyzed. Sample preparation involved crushing and grinding of frozen muscle tissue followed by extraction with an appropriate buffer until a slurry of tissue was obtained. The homogenized tissue was centrifuged at 40,000 x g for 30 minutes at 4-6 °C. The supernatant was collected and stored frozen in 100 µL aliquots until needed.

The samples were analyzed by isoelectric focusing using thin (~300 µm) polyacrylamide gels. Approximately one µL of sample was applied to the gels and electrophoresed for 75 minutes, followed by silver staining for visualization of the protein. Samples were grouped in each run according to either location or size of catch.

Our preliminary data have shown that it is possible to group the squid protein patterns into at least four distinct types. Additionally, we have observed at least two types of banding patterns with direct enzyme staining for phosphoglucosmutase. These differences are now being correlated with the observed biological descriptions, e.g., size, weight, presence of certain marking patterns, etc. These results are expected to help NOAA scientists determine squid species populations in different areas of the ocean. These data then need to be correlated over time to ascertain whether there are local concentrations of certain squid species at particular times of the year.

Future plans on this project will focus on additional enzyme studies including quantitative measurements using laser densitometry to further detect genetic differences.

9. Determination of Pesticides and PCBs in Cod-Liver Oil (15601)

S. N. Chesler, H. X. Gu, R. M. Parris, K. D. Timmons, and S. A. Wise

A commercially available cod-liver oil is being evaluated for use as a Standard Reference Material. Tissue specimens are often analyzed for polychlorinated biphenyl (PCB) and pesticide components. Cod-liver oil may be a useful surrogate for this matrix.

An analytical method has been developed for the determination of pesticides and single PCB congener components in cod-liver oil. The oil sample is extracted and initially cleaned using a dimethylformamide/water-hexane partitioning procedure. Semi-preparative liquid chromatographic (LC) fractionation of the extract yields fractions that are analyzed using high resolution gas chromatography with electron capture detection. An internal standard method of quantification is employed.

Initially, we have targeted four pesticides and seven PCB components as analytes: hexachlorobenzene, 4,4'-DDT, 4,4'-DDE, transnonachlor, and PCB Nos. 44, 99, 153, 138, 180, 170, and 194. Multiple extractions, fractionations, and GC analyses have verified the reproducibility obtainable using the procedure developed for these components. GC/MS analyses were used as a check of the identity of the pesticide components and to verify the number of chlorine substituents of the PCB congeners. We are currently evaluating additional compounds for use as internal standards in this procedure. This material has been analyzed for dioxins by chemists at the Dow Chemical Research Laboratory.

To evaluate the feasibility of using LC as a second analytical method, chromatographic retention data for 70 PCB congeners have been collected using both reversed-phase (RP) and normal-phase (NP) LC. Neither RP nor NP LC showed sufficient selectivity to achieve the required resolution to quantify individual congeners. The data are being evaluated to determine if a combination of the two chromatographic modes can be used to determine selected congeners.

#### 10. Determination of Dioxin in Soils (15601)

S. N. Chesler and R. M. Parris

Analysis of soils for tetrachlorodibenzo-p-dioxins (TCDDs) and tetrachlorodibenzofurans (TCDFs) and of complex matrices, in general, for low ng/g to pg/g levels of organic compounds are areas of much current research activity. We have collected the necessary materials and equipment required to implement the procedure developed at Dow Chemical Research Laboratory for the analysis of TCDD's and TCDF's in soils. The procedure involves the benzene extraction of soil, a three-step column chromatographic clean-up, further fractionation with both reversed and normal-phase HPLC, and analysis using GC/MS.

The chemically modified chromatographic packings have been prepared, cleaned, and activated, and the appropriate collection zones for the chromatographic steps have been determined.

We initially extracted both spiked soil samples and soil blanks. The residues from the column chromatographic clean-up of these extracts have been analyzed using GC/ECD techniques. We can quantitatively analyze these particular soils for 2,3,7,8-TCDD at the 100 pg/g level with GC/ECD and no HPLC fractionation steps. 1,2,3,4-TCDD can be used as an internal standard and additional isomers are being evaluated as standards. Soil samples containing potentially more interferences have been obtained from sites contaminated with oil containing dioxins and sites exposed to Agent Orange & other herbicide formulations. These samples are currently being analyzed.

GC/ECD techniques are being used to monitor method implementation and modification and will be used to measure 2,3,7,8-TCDD in some of chromatographically suitable soil extracts. GC/MS will also be used for quantification of the 2,3,7,8-TCDD in the soil extracts. Accurate measurements by either technique will require the acquisition of particular congeners to demonstrate isomer specific determination of 2,3,7,8-TCDD in these fraction techniques.

11. Development of a Laboratory Data Networking System (15320)

F. R. Guenther

In the past year, an IBM 9000 Computer/Integrator was purchased. This system is capable of collecting up to 4 channels of GC data at 30 Hz each, plus simultaneous recalculation of stored chromatographic data. The processor, a Motorola 68000, has a greater capacity than required for the current task and it was decided to use the system as the core of our laboratory network.

Software was written to integrate Varian 401 integrators, a HP 9825T computer, a Tektronix 4010 graphics terminal, and a HP 7475 six pen plotter into the network. With this system, we can transfer chromatograms from the Varian 401 (or 402) to the IBM and use either commercial chromatography software or our software to reprocess the data.

As with any multi-channel integrator, when more than one channel is in use, several users will want to use the recalculation, display, or plotting functions simultaneously. Thus a software program was written to allow these functions at a graphics terminal, in effect producing a multi-user system. This software allows up to 6 windows to be drawn on the terminal with chromatograms or parts of chromatograms in any or all of the windows. Direct chromatographic comparisons, point-to-point integrations, and retention time determinations can be made. Reproduction quality plots can also be made of chromatograms or of the window plots on the plotter. Formatted reports can also be sent to the HP 9825T for insertion into a data base or for further calculations. An additional alphanumeric terminal can also be connected to run other programs such as a Data Base Management Program or a Linear Regression Program.

Our future plans are to move the multi-user functions to another microcomputer and integrate an additional IBM 9000 into the network to allow up to four external users to run application programs and access data on the chromatographs and computers.

Additionally we are planning to interface the system to the NBS central computer and will utilize the statistical and file handling utilities available on that system to evaluate the chromatographic data.

12. Research on Metal Chelate Columns (26111)

L. A. Alexander, N. Chessick, A. J. Fatiadi, S. A. Margolis, and D. J. Reeder

The objective of this program is to develop solid phase supports which bind metal ions. The metal-chelate supports can then be used to fractionate proteins. The solid supports that we have investigated are styrene divinylbenzene (SDVB) and Sepharose 6B (S6B) to which we have covalently bonded imino-diacetate (IDA) groups. The metal ions are chelated by this functional group.

Between pH 4.5 and 7.2, the metal ions are tightly bound to these supports and the materials exhibit colors characteristic of the bound metal. These metal-chelate supports have been tested for their ability to bind serum proteins and metal-requiring enzymes. We have examined the effects of protein concentration, solvent pH, solvent ionic strength, and solvent metal ion concentration on the affinity of the proteins for the metal chelate support materials.

$\text{Cu}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Co}^{++}$ , and  $\text{Ni}^{++}$  were tested individually. At a pH of 5.5, 50% or less of a serum sample was bound to the metal ion-IDA-SDVB support when it was packed in a column. The amount of protein eluted with each solvent varied with the ion species. Columns with the first three metal ion species retained 22-30% of the total protein under the eluting conditions whereas the last four metal ion species retained less than 10% of the serum proteins. Examination of the ability of the metal-free IDA-SDVB resin to bind serum proteins indicated that the protein fractionation was not significantly different from that obtained with the  $\text{Cu}^{++}$  chelated support. As the protein load on the metal-IDA-SDVB columns was increased, the amount of protein in the third fraction (eluted with the solvent of highest ionic strength) continued to increase while the amount of protein in the second fraction decreased, indicating that the saturation level of the binding sites of the column was being approached. The protein fractions obtained from each column were analyzed by isoelectric focusing on thin layer polyacrylamide gels. Examination of the protein species eluted in each fraction suggested that the composition of the proteins for a given solvent condition was similar for each column and that the unretained fractions contained  $\beta$ -globulins; the second solvent eluted the  $\gamma$ -globulins; and the third solvent contained the  $\alpha$ -globulins.

$\text{Cu}^{++}$ ,  $\text{Ni}^{++}$  and  $\text{Zn}^{++}$  were chelated to separate samples of S6B. These materials were packed in columns and their ability to bind serum proteins was tested. The metal ions fell into two categories:  $\text{Cu}^{++}$ , which strongly bound the proteins at pH 4.65, and  $\text{Ni}^{++}$  and  $\text{Zn}^{++}$  which bound only 40% of the serum proteins at pH 4.65. At pH 7.25, all three columns bound more than 90% of the applied protein. Some of the protein was eluted by increasing the ionic strength of the solvents and the remaining proteins were eluted with increasing concentrations of the metal ion (range 0.01 to 5%). As the pH decreased, the proteins were eluted with solvents of lower ionic strength. There appeared to be no saturation at the protein concentrations at which this was observed with the SDVB columns. Alkaline phosphatase (a  $\text{Zn}^{++}$  requiring enzyme) did not appear to be retained by the  $\text{Zn}^{++}$  column at the three pH's tested. Similar results were obtained for urease (a  $\text{Ni}^{++}$  requiring enzyme) on a  $\text{Ni}^{++}$  column.

The results obtained in these experiments indicate that the metal ions modify the affinity of these supports for serum proteins. The degree of modification appears to be minimal for the SDVB support. In the case of the S6B support, the modification is more significant. The inability of these columns to bind specific metal-requiring enzymes, combined with the ability of increasing concentrations of the metal ions to elute the bound serum proteins, suggests that the fundamental mechanism of separation may be ion exchange.

13. Influence of Physical and Chemical Parameters of Silica Substrates on the Reversed-Phase Liquid Chromatographic Performance of Alkyl Bonded Phases (15320)

L. C. Sander and S. A. Wise

Reversed-phase chromatography on chemically bonded octadecylsilane ( $C_{18}$ ) stationary phases is by far the most popular separation mode currently in use in liquid chromatography. Understandably, the study of these phases is an area of considerable interest, both from theoretical and from practical points of view. Much of this interest is a result of differences in retention and selectivity that exist among columns of the same phase type. In earlier work, differences between monomeric, oligomeric, and polymeric  $C_{18}$  phases were examined for narrow and wide pore substrates. In our current research, changes in chromatographic performance were examined as a function of physical and chemical properties of the silica substrate. An understanding of these effects may be valuable in explaining differences among commercial columns, and ultimately, in tailoring bonded phases for a specific separation problem.

A total of 22 different silica substrates, with nominal pore sizes ranging from 50-1000 Å (5-100 nm), were used in the preparation of the bonded phases investigated in this study. Surface areas of these substrates, measured by nitrogen adsorption, ranged from 32-433 m<sup>2</sup>/g. Polymeric phases were synthesized on each of these substrates under controlled conditions. The resulting surface coverage values increased with increasing substrate pore size. Polycyclic aromatic hydrocarbons (PAH) were used to evaluate the chromatographic properties of the phases. In general, phases prepared on wide pore substrates were more selective toward PAH, and better separations of PAH were obtained than with narrow pore substrates. These differences are attributed to a size exclusion mechanism during the bonded phase synthesis that limits polymeric phase coverage with narrow pore substrates.

Substrate effects were further studied by synthesizing monomeric and polymeric phases on silica pretreated with hydrochloric acid or sodium hydroxide. No significant differences were observed in the chromatographic properties of monomeric  $C_{18}$  phases prepared on acid washed, base washed, or untreated silica. However, with polymeric phase modification, differences in phase loading and column selectivity were noted, with the greatest polymeric character occurring for the acid treated silica.

Although phase reproducibility is readily controlled for a given silica substrate, the results of this study demonstrate clearly that large variations in phase loading and column performance may result when syntheses are performed on different substrates. Pore size and acid/base pretreatment are

two parameters that have been observed to affect bonded phase syntheses; other substrate parameters such as trace metal composition, not considered in this study, may further influence phase characteristics and work in this area continues.

14. Optimization of Secondary Chemical Equilibria in Liquid Chromatography (27201)

J. P. Foley and W. E. May

Conventional modern liquid chromatography (LC) uses "primary" chemical equilibria, i.e., bulk mobile phase $\rightarrow$ solute interactions and solute $\rightarrow$ stationary phase interactions, to separate the analytes of interest. Other secondary chemical equilibria (SCE) involving the analytes and the mobile or stationary phase, i.e., acid $\rightarrow$ base dissociation, complex formation, etc., are usually deemed undesirable and are suppressed so that each analyte is eluted in one chemical form.

When analytes cannot be readily separated via conventional LC, SCE can and should be employed, if possible. With SCE $\rightarrow$ LC, the mobile phase is chosen to provide an environment in which the analytes now exist in two or more chromatographically distinct forms. Although seemingly paradoxical, it is nevertheless true that separations exploiting the analytes' SCE usually succeed in instances where suppressing the SCE results in failure.

Although previous separations utilizing SCE $\rightarrow$ LC have been successful, conditions for optimum resolution have been found mainly by trial $\rightarrow$ and $\rightarrow$ error or by empirical optimization strategies. The purpose of the present study is to examine SCE $\rightarrow$ LC from a fundamental point of view to develop an a priori theory that predicts and explains the optimum isocratic mobile phase for the separation of interest. The potential rewards are superior SCE $\rightarrow$ LC separations, in terms of reduced analysis times for separations currently being performed, the ability to perform separations of previously unresolved compounds in complex mixtures, and additional knowledge about retention mechanisms in SCE $\rightarrow$ LC systems.

Because column efficiencies have frequently been lower when aqueous SCE $\rightarrow$ LC has been employed, one goal was to increase the efficiency of aqueous SCE $\rightarrow$ LC systems to levels which equaled that of conventional reversed $\rightarrow$ phase liquid chromatography (RPLC). We hypothesized that small amounts of the appropriate organic solvent, when added to the aqueous mobile phase, will "wet" the nonpolar stationary phase, thus improving the mass transfer sufficiently to achieve this goal. Methanol, ethanol, n $\rightarrow$ propanol, and acetonitrile were selected to test this hypothesis.

Our results show that n $\rightarrow$ propanol was by far the most effective organic solvent, with 3 $\rightarrow$ 6% (by volume) improving chromatographic efficiencies by factors of 10 $\rightarrow$ 15, which approaches efficiencies observed in conventional RPLC. Only slight improvements were observed with the other solvents.

More fundamental than the efficiency improvements we achieved is the optimization of the selectivity (relative retention) in SCE $\rightarrow$ LC. Improvements in selectivity can provide dramatic increases in resolution and/or large reductions in analysis times.

Our theoretical investigation of selectivity-optimized SCE-LC is based on a well established retention model in which the overall retention of an analyte is given by the weighted average of the retentions of its various forms. Our results are summarized below:

1. Simple equations which predict the optimum mobile phase conditions have been derived for all SCE-LC systems in which each of a pair of analytes is limited to two forms (dimorphic).
2. Although it was not feasible to derive explicit equations for the polymorphic (3 or more forms) cases due to the algebraic complexity of the expressions, it was possible to predict, via simulation, the number and locations of the mobile phase optima.
3. In most instances, the selectivity we predicted was significantly higher than previous selectivity predictions, suggesting that the power of SCE-LC has been substantially underestimated.

Our experiments to date have focused on acid-base equilibria in reversed-phase systems at low to moderate ionic strengths ( $< 0.03$ ). Benzoic acid and some simple derivatives have been used most extensively as test solutes. Our results may be summarized as follows:

1. The retention model on which our SCE-LC theory and simulations are based was experimentally verified for the acid-base systems we examined. Thus our theory is valid for these systems.
2. The self-selectivities [relative retentions of the two forms of the analyte, i.e.,  $k(\text{form 1})/k(\text{form 2})$ ] of the ortho-substituted benzoic acid isomers were found to be significantly higher than for the corresponding meta- and para-isomers. This may be due to intramolecular H-bonding effects and will be investigated further.
3. The self-selectivities of the substituted benzoic acids varied considerably from one column to another. Therefore some columns will be better for a given SCE-LC application than others.

All the results discussed in this report apply to isocratic chromatographic systems. Some additional experimental verification of the theory for dimorphic analytes is needed, as well as a more thorough analysis for polymorphic systems, before this part of the study is concluded. Following this, we plan to pursue the optimization of selectivity in gradient SCE-LC systems.

#### 15. Quantitative Analysis of Complex Mixtures by LC/MS/MS

R. G. Christensen and E. White V

Quantitative trace analysis for organic compounds in complex matrices often requires time-consuming and laborious sample preparation. These manipulations, in addition to lengthening the analysis time, can lead to the introduction of systematic errors. The combination of a liquid chromatograph with a mass spectrometer (LC/MS) has been used in this laboratory to perform

such analyses without sample pretreatment. In some analyses, however, interferences arise which cannot be resolved by either the liquid chromatographic separation or by the selectivity of the mass spectrometer.

The technique of tandem mass spectrometry (MS/MS) with collision-induced dissociation offers an additional degree of selectivity. This is accomplished by separating all the ions of a mass corresponding to the mass of the ion species of interest and subjecting these ions to collision with gas molecules. A second mass analyzer is then used to scan for fragment ions specific to the ion of interest.

We have used this method to quantify dibenzothiophene in two oil matrices, i.e., SRM 1582 (a petroleum crude oil) and SRC-II (a solvent-refined coal liquid). A conventional liquid chromatograph was used in the normal-phase mode, coupled to a triple quadrupole mass spectrometer by a preconcentrating interface of our own design. Since dibenzothiophene was found to lose sulfur on collision with nitrogen molecules, the first filtering quadrupole was set to mass  $m/z$  184 (corresponding to  $M^+$  for dibenzothiophene) and the second for  $m/z$  152 (corresponding to neutral loss of sulfur). The peak heights in ion current vs. time for oil samples were compared to those from the injection of external standards. Results agreed with determinations by other, more laborious methods. For example, the dibenzothiophene content of a solvent-refined coal liquid was found to be  $1017 \pm 78 \mu\text{g/mL}$ , compared to  $1020 \pm 70 \mu\text{g/mL}$  by GC/MS.

Using this method, the time required for each chromatographic run was only 7 minutes and the detection limit for dibenzothiophene was less than 20 ng. Thus the combination of LC/MS/MS provides a rapid and fairly sensitive means of determining dibenzothiophene in oil matrices with no sample pretreatment except an appropriate dilution.

#### 16. Thermal Crosslinking Procedure for Preparing Solvent-Stable Polymer-Film Electrodes (26101)

E. A. Blubaugh

Our immediate interest in chemically modified electrodes is in the utilization of these electrocatalytic surfaces as selective and sensitive analytical electrochemical detectors (LCEC) for liquid chromatography.

Published literature procedures for polymer film electrodes gave results which were unsatisfactory. The major problems resulted from instability found for the film/electrode interfaces or dissolution of the film. We have developed a thermal crosslinking procedure that yields a solvent stable film and, in addition, a stable film/electrode interface.

The polymer was cast onto a 5 mm diameter superficially oxidized platinum disc electrode surface from a 1 percent (W/W) methanol solution of polyvinylpyridine/styrene copolymer (9:1), with benzoyl peroxide and triallyltrimellitate (e.g., 5%, 10%, or 20% crosslinking agent). An aliquot of the solution was pipetted onto the prepared electrode. Evaporating the methanol leaves a polymeric gel on the surface of the electrode. This polymeric gel was heated, transforming the gel into a transparent film. These polymer film electrodes were heat cured at 95 °C for 2.5 hours.



The polymer film electrodes prepared in this manner show an enhanced stability toward a variety of solvents (polar or nonpolar) relative to the conventional 4-vinylpyridine/styrene copolymer. This stability is a result of the thermosetting and crosslinking of the polymer film on the electrode surface.

These polymer film electrodes can be used to immobilize a variety of catalyst molecules and use of these electrodes for the catalytic reduction of organohalides will be discussed elsewhere. Further studies will be directed towards the characterization of polymer film electrodes containing the different catalyst molecules.

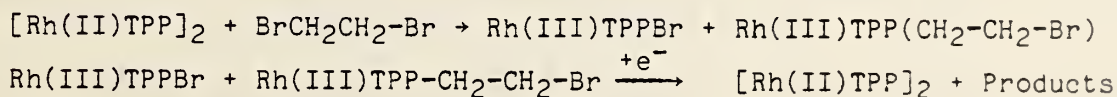
17. Electrocatalytic Reduction of Ethylene Dibromide via Rhodium(II) Tetraphenylporphyrin Dimer Derivatized Polymer Film Electrodes (26101)

E. A. Blubaugh

A variety of organometallic/transition metal complexes have been immobilized within the solvent stable polyvinyl pyridine/styrene copolymer (PVP/styrene) modified film electrodes. We will focus on the chemical immobilization of rhodium(II) tetraphenylporphyrin [Rh(III)TPP] dimer complexes, with their concomitant ability to reduce organohalides catalytically.

The preparation of rhodium(II) tetraphenylporphyrin is easily accomplished by the reduction of rhodium(III) tetraphenylporphyrin chloride, via sodium borohydride and subsequent removal of the benzene solvent. These dimer complexes can be immobilized in the previously prepared PVP/styrene film electrodes by immersion of the electrodes in a benzene solution of the dimer.

There is no observed electroactivity for these dimer derivatized electrodes in the potential window of  $\pm 2$  volts versus the saturated sodium calomel reference electrode (S.S.C.E). However, when an aliquot of ethylene dibromide is added (making the solution  $\sim 10^{-6}$  M in EDB), there are two reduction processes observed at -1.325 volts and -1.677 volts versus S.S.C.E. These peak potentials agree with the reduction potentials for rhodium(III) tetraphenylporphyrin Br and rhodium(III) tetraphenylprophyrin  $\text{CH}_2\text{-CH}_2\text{-Br}$  (via separate solution electrochemical studies). We propose the following reaction scheme to describe the chemical process occurring in the film:



The catalytic mechanism is completed by the electrode reducing the rhodium(III) species to rhodium(II) followed by dimer reformation.

These results are exciting for two reasons. The first is that alkyl bromo species are not reduced until potentials more negative than -2.00 volts vs S.S.C.E are reached (at unmodified electrodes). Our modified electrodes catalytically reduce the bromo alkyl species at -1.677 volts or less. The second reason is that these modified electrodes do not respond to aryl bromo species, such as bromobenzene, giving a selectivity between alkyl and aryl

bromo organic compounds. Future work will be directed towards further characterization of the rhodium $\rightarrow$ dimer complex to determine the properties of the individual species involved in the catalytic reactions within the film.

18. Refinement of the Mathematical Model for Charge Transport in Polymer $\rightarrow$ Film Electrodes (26101)

E. A. Blubaugh, R. A. Durst, and W. T. Yap

In an attempt to explain observed deviations from diffusion $\rightarrow$ controlled behavior, we had previously developed a model for charge transport through polymer films on chemically modified electrodes by considering both diffusion of the electroactive group due to the concentration gradient in the polymer film and the migration of charged groups caused by a constant electric field across the film [1]. The current $\rightarrow$ time relationship for chronoamperometry was derived analytically for this very simple first model. The characteristic  $i \cdot t^{1/2}$  versus  $t^{1/2}$  plots obtained for migration $\rightarrow$ enhanced charge diffusion closely described several known systems of polymer $\rightarrow$ modified electrodes where Cottrell (ideal diffusional) behavior is not followed. In addition, our model predicts behavior where the charge transport by migration opposes that of diffusion and results in an initial decrease in the  $i \cdot t^{1/2}$  vs.  $t^{1/2}$  plots for chronoamperometric experiments. Polymer $\rightarrow$ film systems which exhibit this type of behavior will be investigated to confirm our electromigration model. We are also modifying the charge $\rightarrow$ transport model to predict the effects of changes in the experimental parameters.

In the latest refinement of the migration model, we are investigating the effect of allowing the electric field to decrease with time until it reaches a zero field gradient at steady state instead of the constant electric field across the polymer film as previously assumed. Since this modification makes the model too complicated to solve analytically, we are using numerical simulations to obtain the current $\rightarrow$ time relationships. As expected, the overall shapes of the current $\rightarrow$ time plots change little. Only the magnitude of the current deviations from Cottrell behavior is progressively reduced as a result of the decrease in the electric field gradient with time.

The non $\rightarrow$ faradaic process of charging the polymer film, which acts as a capacitance, will also produce an enhancement to the observed current. Therefore, we are also modeling by numerical simulation the effects of film capacitance and resistance on the current $\rightarrow$ time plots. Preliminary results show that charging currents due to capacitance and resistance effects (i.e., RC time constant of the film) also produce  $i \cdot t^{1/2}$  vs.  $t^{1/2}$  plots which have positive initial slopes (in contrast to the zero slope for Cottrell behavior) as in the case of migration enhancement. However, the finer features of these plots are quite different in the two cases, and we are studying these in more detail, both experimentally and theoretically.

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19. Electrochemical Characterization of a Series of Metal-Dithiosquarate Complexes (27202)

G. S. Marbury

There has been considerable interest in dithiolene ligands with strongly electron-withdrawing properties since these tend to stabilize lower, sometimes uncommon, oxidation states of the central metal ion. Generally all dithiolene complexes exhibit multiple states related by reversible one-electron transfer reactions, the ease of which can be related to the electron-withdrawing ability of the ligand (and attached substituent groups). Maleonitrile dithiolate had been the most strongly electron-withdrawing of the dithiolene ligands. Recently, however, oxocarbon derivatives have been synthesized which exhibit greater electron-withdrawing character.

Preliminary studies with nickel showed that the order for ease of reduction with the newer dithiolene ligands to be: dicyanomethylene-dithiocroconate, dithiocroconate, and dithiosquarate. Of these ligands, the dithiosquarate was chosen for detailed study because of its steric constraints. Complexes of this ligand with five different transition metals (Cu, Ni, Pt, Pd, and Au) were characterized electrochemically in dimethylformamide. Cyclic voltammetric studies show the redox couples in the complexes to be quasi-reversible in nature. The diffusion coefficients calculated from chronocoulometric data follow the expected trend of increasing with the size of the complex.

Because of the absence of useable spectral characteristics,  $E^{\circ}$  and  $n$  values could not be determined spectroelectrochemically. Since thin-layer pulse-coulometry is an alternative technique for determining the  $E^{\circ}$  and  $n$  values for complexes with low extinction coefficients, we plan to include this technique in the study of all the dithiosquarate complexes.

20. Preparation and Characterization of Reference Materials for EPA's Water and Hazardous Waste Programs (15320)

J. M. Brown-Thomas, G. D. Byrd, S. N. Chesler, R. B. Christensen, F. R. Guenther, L.R. Hilpert, W. F. Kline, W. A. MacCrehan, W. E. May, M. M. Miller, R. E. Rebbert, D. J. Reeder, and L. T. Sniegowski

During the past several years, we have supported the Quality Assurance Programs of the Environmental Protection Agency. Work during the past year has focused on the preparation of Reference Materials in the following areas:

1. Preparation of a Quality Assurance Solid Sludge Material for Hazardous Waste Measurements

We have prepared and analyzed a quality assurance solid sludge material for the Environmental Protection Agency in conjunction with the Inorganic Analytical Research Division. Our objective was to identify and quantify several organic compounds, most of which are priority pollutants, in an actual composite solid sludge and in aqueous leachates of that material. The experimental plan for sampling and analysis was designed using accepted statistical procedures to enable us to analyze the components of variability contributed by the sample itself, the work-up procedure, and the GC/MS measurement step. Aqueous leachates of the composite sludge were prepared

and analyzed according to standard EPA procedures. The concentrations of analytes in the aqueous leachates were in the 1-100 part-per-billion range. The results of the study showed that the variabilities of the work-up procedure and GC/MS measurements were major contributors to the overall uncertainty in the determined values. Approximately 100 units of the solid sludge material were delivered to the EPA Environmental Monitoring and Support Laboratory, Las Vegas, NV.

## 2. Preparation of a Synthetic Urine Reference Material Containing Phenolic Compounds and Plasticizers

A synthetic urine reference material was prepared by fortifying a base material containing electrolytes, nitrogenous substances, and other components normally found in urine with 2,4,5-trichlorophenol, pentachlorophenol, phenol, p-nitrophenol, bis(2-ethylhexyl)phthalate and bis(2-ethylhexyl)adipate at a range of concentrations between 0.1 and 5 ppm. The gravimetric concentrations of the phenols were verified and stability measurements conducted using liquid chromatography. The initial concentrations of the esters were approximately 0.1 ppm and decreased with time due to adsorptive losses on the container walls. One hundred & fifty units of the reference material and 400 units of the base stock were delivered to the EPA Environmental Monitoring and Support Laboratory in Las Vegas, NV.

## 3. Preparation of a Human Serum Reference Material Containing Polychlorinated Biphenyls

A set of human serum samples containing known amounts of polychlorinated biphenyls (PCB's) have been prepared for use as reference materials. The human serum, which was obtained commercially, was stripped of low molecular weight contaminants by charcoal filtration. The PCB's were added gravimetrically as a commercial mixture, Aroclor 1260 (60% chlorine by weight), at two concentration levels: 10 ng/g and 50 ng/g. These levels represent the high-normal and toxic levels of PCB's found in the human population. Measurements of the PCB concentrations were made by gas chromatography to confirm the gravimetric values. The measured values were  $11.2 \pm 0.4$  ng/g and  $60.0 \pm 1.3$  ng/g. Three hundred samples at each concentration level, as well as a serum blank, were prepared and will be delivered to the EPA EMSL laboratory in Las Vegas, NV.

## 4. Analysis of EPA Calibration and Performance Evaluation Samples.

This work was undertaken as part of the Center for Analytical Chemistry's effort to assist EPA's Quality Assurance Branch in Cincinnati by providing NBS traceability on their calibration solution standards and on quality assurance samples prepared by outside contractors. The following samples were analyzed by gas chromatography with electron capture or flame ionization detection: "Volatile Organics" (nine halocarbons in methanol); "Trihalomethanes" (chloroform, bromoform, bromodichloromethane and dibromochloromethane in methanol); "Chlorinated Hydrocarbon Pesticides" (lindane, endrin, methoxychlor in acetone). "Temik" samples (aldicarb, aldicarb sulfone, and aldicarb sulfoxide in acetonitrile) were analyzed by liquid chromatography with both UV detection and fluorescence detection after post column derivitization. "Trace Metals" (26 trace metals in water) were analyzed in the Inorganic Analytical Research Division by inductively coupled plasma spectrometry and one of several other techniques which included Atomic

Absorption Spectroscopy, Flame Emission Spectroscopy, Laser Enhanced Ionization Spectroscopy, Direct Current Plasma Emission Spectroscopy, and Neutron Activation Analysis.

At this point, NBS Reports of Analysis are used as the means for establishing traceability. The Center is currently in the process of drafting a document that provides a definition of "traceability".

21. Certification of a Priority Pollutant Phenols in Methanol SRM (15602)

J. M. Brown-Thomas, S. N. Chesler, D. K. Hancock, W. F. Kline, W. E. May, R. M. Parris, and R. E. Rebbert

Certification of SRM 1584, Priority Pollutant Phenols in Methanol, has been completed. The SRM was prepared in-house and contains the eleven phenols included on the EPA's List of Priority Pollutants. The SRM is intended primarily for use in calibrating chromatographic instrumentation used in the determination of phenols and, because of its miscibility with water, can also be used to fortify aqueous samples with known concentrations of phenols. The individual phenolic compounds in the SRM are: 2-nitrophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; 4-nitrophenol; pentachlorophenol; 4-chloro-m-cresol; 4,6-dinitro-o-cresol; 2,4-dinitrophenol; o-chlorophenol and 2,4 dimethylphenol.

Randomly selected samples were analyzed for four of the eleven phenols by HPLC on a reversed-phase C-3 (5  $\mu\text{m}$ ) column using an aqueous acetic acid/acetonitrile/methanol mobile phase and UV detection at 254 nm. Four external standard solutions were used to provide response factors for HPLC quantification. Seven of the eleven compounds were determined by gas chromatographic (GC) analysis on a fused silica OV-1701 capillary column with flame ionization detection. Four independent GC calibration solutions were used to obtain responses relative to 6-chloro-m-cresol, the internal standard. The gravimetric concentrations were calculated from the mass of each phenolic compound added to a known mass of methanol in the preparation of the SRM.

The certified values for the concentrations of ten of the phenols were determined from the concordant results of two independent analytical techniques. The information value provided for 2,4-dinitrophenol is based only on the results from HPLC analyses, but with UV detection at both 254 and 290 nm. The SRM is available through the Office of Standard Reference Materials.

22. Certification of a Diesel Particulate SRM (15320)

H. X. Gu, L. R. Hilpert, W. F. Kline, W. A. MacCrehan, and W. E. May

It is generally thought that the increasing use of diesel engines poses a potential human health risk. Organic solvent extracts of diesel exhaust particulates exhibit direct acting mutagenicity in the Ames test [1-3]. In addition, diesel engines produce 50-80 times more particles than catalyst equipped spark ignition engines, with the diameters of the agglomerated particles being typically less than 1  $\mu\text{m}$ . Particles in this size range are thought to be extremely harmful to humans because they may be respired and deposited in the lungs [4]. Because of these reasons, there has been a great deal of interest in the analytical characterization of organic components on

great deal of interest in the analytical characterization of organic components on diesel exhaust particulate matter. The Department of Defense, Department of Energy, Environmental Protection Agency, and Coordinating Research Council are all funding contract research in this area.

The major organic components in diesel exhaust particulates appear to be the polynuclear aromatic hydrocarbons (PAH). The PAH have been found to exhibit less than 5 percent of the direct-acting mutagenicity associated with organic extracts of diesel particulate matter [2].

Diesel particulate extracts have also been found to contain several PAH derivatives, including hydroxy, dihydroxy, keto, quinone, carboxaldehyde, acid anhydride, and nitro substituents. Of these, the nitro-PAH are thought to be the most active.

During the past year we have measured the concentrations of a number of PAH and nitrated PAH on a diesel exhaust particulate sample donated by the Coordinating Research Council Inc., Atlanta, GA. by at least two methods each. The PAH were determined by LC-fluorescence and GC/MS after soxhlet extraction with methylene chloride and methanol/toluene respectively. The nitrated PAH were determined by soxhlet extraction and either LC-fluorescence after on-line reduction to the corresponding amine, soxhlet extraction followed by GC/MS, or ultrasonic extraction and LC with reductive electrochemical detection.

The SRM is being packaged as units consisting of three 100 mg ampoules and should be available in late fall after statistical analysis of the data has been completed.

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- [2] Pepelko, W. E.; Donner, R. M.; Clarke, N. A., Eds. "Health Effects of Diesel Engine Emissions: Proceedings of an International Symposium, Dec 3-5, 1979; U.S. Environmental Agency: Cincinnati, OH, 1980; EPA-600/9-80-057.
- [3] Huisingh, J.; Bradow, R.; Jungers, R.; Claxton, L.; Zwiedinger, R.; Tejada, S.; Bumgarner, J.; Duffield, F.; Waters, M.; Simmon, V. F.; Hare, C.; Rodriguez, C.; Snow, L. M. "Application of Short Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures"; Waters, M. D.; Nesnow, S.; Huisingh, J.; Sandu, S.; Claxton, L., Eds.; Plenum Press: New York, 1978; EPA-600/9-78-027.
- [4] Chan, T. L.; Lee, P. S.; Hering, W. E. *JAT*, J. Appl. Toxicol. 1981, 1, 77-82.

23. Certification of a Gas Chromatography/Mass Spectrometry Performance SRM (26108)

J. M. Brown-Thomas, S. N. Chesler, R. G. Christensen, L. R. Hilpert, R. C. Paule (500), R. E. Rebbert, L. T. Sniegowski, and E. White V.

This SRM is the first of a possible series intended to provide materials suitable for testing the performance of analytical instruments. Gas chromatography/mass spectrometry (GC/MS) was selected as a suitable test case. Since there are only a few U.S. manufacturers of GC/MS instruments, most use the same test compounds. However, both manufacturers and end users must prepare their own test materials.

SRM 1543 provides materials with certified concentrations of two compounds most commonly used to test the sensitivity of gas chromatography/mass spectrometer systems. It will provide instrument manufacturers and their customers with an independent source of test samples for evaluating instrument performance.

Certification was based on the gravimetric values from the preparation of the SRM as well as analytical values determined by gas chromatography. The SRM, as issued, consists of 1 mL of each of four hexane solutions. The material and certified values are; methyl stearate at  $0.99 \pm .02$  ng/ $\mu$ L, methyl stearate at  $4.98 \pm .08$  ng/ $\mu$ L, benzophenone at  $1.01 \pm .02$  ng/ $\mu$ L, and benzophenone at  $5.01 \pm .07$  ng/ $\mu$ L. The certified values are valid between 18 °C and 28 °C.

C. Outputs and Interactions  
(Organic Analytical Research Division)

1. Publications

- Bunding, K. A., Durst, R. A., and Bell, M. I., Surface-Enhanced Raman Spectroscopy of N-Methylpyridinium Cation and Pyridine: Identification of Surface Species, *J. Electroanal. Chem.* 150, 437-446 (1983).
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- Coxon, B., Two-Dimensional J-Resolved Proton Nuclear Magnetic Resonance Spectroscopy of Hydroxyl Proton Coupled  $\alpha$ - and  $\beta$ -D-Glucose, *Anal. Chem.* 55, 2361 (1983).
- Elder, R. C., Blubaugh, E. A., Heineman, W. R., Burke, P. J., and McMillin, D. R., Thin-Layer Spectroelectrochemical Studies of Copper and Nickel Unsymmetrical Schiff Base Complexes, *Inorg. Chem.* 22, 2777 (1983).
- Fultz, M. L. and Durst, R. A., Investigation of Two Multichannel Image Detectors for Use in Spectroelectrochemistry, *Talanta* 30, 933-939 (1983).
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- Mayfield, H. T. and Bertsch, W., An Algorithm for Rapidly Organizing Gas Chromatographic Data into Data Sets for Chemometric Analysis, *J. Computer Applications in the Lab.* 1, 130-136 (1983).
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- Foley, J. P. and Dorsey, J. G., A Review of the Exponentially Modified Gaussian (EMG): Evaluation and Subsequent Calculation of Universal Data, *J. Chromatog. Sci.* 22, 40-46 (1984).
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- Blubaugh, E. A., Chiang, C. K., and Yap, W. T., Electrochemical Behavior of Doped Polyacetylene Films, *J. Electroanal. Chem.*, in press.
- Botto, R. E. and Coxon, B., Two-Dimensional Proton J-Resolved NMR Spectroscopy of Neomycin B, *J. Carbohydr. Chem.*, in press.

- Burke, R. T., Blubaugh, E. A., Yap, W. T., and Durst, R. A., Electrochemical Investigation of N-Methyl-4-(5-phenyl-2-oxazolyl)pyridinium p-Toluene-sulfonate, *J. Electroanal. Chem.*, in press.
- Coxon, B., Two-Dimensional Proton Chemical Shift Correlated NMR Spectroscopy of Digitoxose, *J. Carbohydr. Chem.*, in press.
- Durst, R. A., Clinical Electrode Potentiometry: Sources of Error, Reference Methods and Materials, Direct Potentiometric Measurements in Blood, W. Koch, ed., in press.
- Fatiadi, A. J., New Applications of Tetracyanoethylene in Organic Chemistry, Synthesis, in press.
- Fatiadi, A. J., The Oxidation of Organic Compounds by Active Manganese Dioxide, Oxidative Procedures in Org. Chem. Involving Metal Compounds, W. J. Mijs, ed., Plenum Press, London, in press.
- Fatiadi, A. J., Priority Toxic Pollutants in Human Urine: Their Occurrence and Analysis, *Environment International*, in press.
- Fletcher, R. A. and Fatiadi, A. J., Laser Ionization Mass Spectrometry of Poly(4-Vinylpyridine), *Anal. Chem.*, in press.
- Foley, J. P. and Dorsey, J. G., Clarification of the Limit of Detection in Chromatography, *Chromatographia*, in press.
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- Margolis, S. A. and Coxon, B., Amino Acid Analysis of Angiotensin I by Proton NMR Spectroscopy, *Anal. Biochem.*, in press.
- Mattammal, M. B., White V, E., Zenser, T. V., and Davis, B. B., Mass Spectrometry of 2-Substituted-Y-Arylthiazoles. III. Identification of Microsomal Nitroreduction Products by Mass Spectrometry, *Biomed. Mass Spectrom.*, in press.
- Sander, L. C. and Wise, S. A., The Influence of Substrate Parameters on Column Selectivity with Alkyl Bonded-Phase Sorbents, *J. Chromatog.*, in press.
- Sander, L. C. and Wise, S. A., Synthesis and Characterization of C<sub>18</sub> Stationary Phases for the Liquid Chromatographic Separation of Polycyclic Aromatic Hydrocarbons, in *Proc. 8th Internatl. Sym. on Polynuclear Aromatic Hydrocarbons*, Columbus, OH, October 1983, in press.

- Wasik, S. P., Schwarz, F. P., Tewari, Y. B., Miller, M. M., and Purnell, J. H., A Head-Space Method for Measuring Activity Coefficients, Partition Coefficients, and Solubilities of Hydrocarbons in Aqueous Solutions, NBS J. Res., in press.
- Wise, S. A., Analytical Techniques for the Determination of Petroleum Hydrocarbons and Combustion Products, in Pollution and the Protection of Water Quality, R. W. Risebrough, ed., Hemisphere Publishing, New York, in press.
- Wise, S. A., Interlaboratory Comparisons and the Use of Reference Materials for Quality Control of Analytical Methodologies, in Pollution and the Protection of Water Quality, R. W. Risebrough, ed., Hemisphere Publishing, New York, in press.
- Wise, S. A., Recent Progress in the Determination of Polycyclic Aromatic Hydrocarbons by High-Performance Liquid Chromatography, in Handbook for Polycyclic Aromatic Hydrocarbons: Volume II, A. Bjørseth and T. Ramdahl, eds., Marcel Dekker, New York, NY, in press.
- Wise, S. A., Chesler, S. N., Hilpert, L. R., May, W. E., Rebbert, R. E., and Vogt, C. R., Characterization of Polycyclic Aromatic Hydrocarbon Mixtures from Air Particulate Samples Using Liquid Chromatography, Gas Chromatography, and Mass Spectrometry, in Proc. 8th Internatl. Sym. on Polynuclear Aromatic Hydrocarbons, Columbus, OH, October 1983, in press.
- Wise, S. A. and Zeisler, R., The Pilot Environmental Specimen Bank Program, Environ. Sci. Technol., in press.
- Zeisler, R. and Wise, S. A., Quality Assurance and Protocols in Sampling and Sample Preparation of Biological Samples, in Proc. Internatl. Sym. Biol. Ref. Matls. for Nut. Anal., Philadelphia, PA, September 1983, in press.

## 2. Talks

- S. A. Wise, "Standard Reference Materials for Trace Organic Analysis," Fourth Ulmer Symposium on Analytical Chemistry, University of Ulm, Ulm, Germany, October 6, 1983. Invited
- R. A. Durst, "Novel Approaches to Organic Electroanalysis," Analytical/Nuclear/Environmental Division Seminar, University of Maryland, College Park, MD, October 21, 1983. Invited
- J. M. Brown-Thomas, "Analysis of Organic Nutrients by High-Performance Liquid Chromatography," Third NBS/ADABSE Analytical Chemistry Workshop, NBS, Gaithersburg, MD, October 25, 1983.
- L. C. Sander, "Theory and Practice of High-Performance Liquid Chromatography," Third NBS/ADABSE Analytical Chemistry Workshop, NBS, Gaithersburg, MD, October 25, 1983.

- W. A. MacCrehan, "Determination of Nitro-Polynuclear Aromatic Hydrocarbons in Diesel Soot by Liquid Chromatography with Fluorescence and Electrochemical Detection," Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Laboratories, Columbus, OH, October 27, 1983.
- S. A. Wise, "Characterization of Polycyclic Aromatic Hydrocarbon Mixtures from Air Particulate Samples Using Liquid Chromatography, Gas Chromatography, and Mass Spectrometry," Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH, October 27, 1983.
- E. A. Blubaugh, "Electrochemical Techniques: Cyclic Voltammetry and Hybrid Electrochemical Techniques," Third NBS/ADABSE Analytical Chemistry Workshop, NBS, Gaithersburg, MD, October 28, 1983.
- S. N. Chesler, "Gas Chromatography," Third NBS/ADABSE Analytical Chemistry Workshop, NBS, Gaithersburg, MD, October 28, 1983.
- B. Coxon, "Two-Dimensional NMR Spectroscopy," Third NBS/ADABSE Analytical Chemistry Workshop, NBS, Gaithersburg, MD, October 28, 1983. Invited
- D. J. Reeder, "Two-Dimensional Electrophoresis," Third NBS/ADABSE Analytical Chemistry Workshop, NBS, Gaithersburg, MD, October 28, 1983.
- S. A. Wise, "Synthesis and Characterization of C<sub>18</sub> Stationary Phases for the Liquid Chromatographic Separation of Polycyclic Aromatic Hydrocarbons," Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH, October 28, 1983.
- L. R. Hilpert, "Selectivity of Detection for Benzo[a]pyrene and Other PAH Using Negative Ion Chemical Ionization Mass Spectrometry," NBS/DOE Analytical Characterization Group Meeting, Ames, IA, November 2, 1983. Invited
- W. E. May, "High-Performance Liquid Chromatographic Determination of Nitrated-Polynuclear Aromatic Hydrocarbons in Complex Mixtures," 35th Southeast Regional Meeting of the American Chemical Society, Charlotte, NC, November 9, 1983. Invited
- E. White V, "Isotope Dilution GC/MS Applied to Clinical Chemistry," Department of Chemistry, University of Maryland, College Park, MD, November 18, 1983. Invited
- R. G. Christensen, "LC/MS with Continuous Preconcentration," Analytical Seminar, Chemistry Department, University of Nebraska-Lincoln, Lincoln, NE, November 21, 1983. Invited
- B. Coxon, "Two-Dimensional NMR Spectroscopy," Towson State University, Towson, MD, December 16, 1983. Invited
- W. A. MacCrehan, "Adventures in LCEC," Washington Chromatography Discussion Group, Rockville, MD, January 19, 1984. Invited

- E. A. Blubaugh, "Spectroelectrochemistry of a System with Product Deposition," Gordon Research Conference on Electrochemistry, Santa Barbara, CA, January 24, 1984.
- R. A. Durst, "Electrochemical/Spectroelectrochemical Investigation of N-Methyl-4-(5-phenyl-2-oxazolyl)pyridinium p-Toluenesulfonate Laser Dye," Gordon Research Conference on Electrochemistry, Santa Barbara, CA, January 24, 1984.
- R. A. Durst, "Electrochemical Approaches to Organic Analysis," McGill University Chemical Society, Montreal, Canada, February 7, 1984. Invited
- D. K. Hancock, "Characterization of Proteins by Two-Dimensional Electrophoresis," Washington Chromatography Discussion Group, February 16, 1984. Invited
- B. Coxon, "Two-Dimensional NMR Spectroscopy of Carbohydrates," Villanova University, Villanova, PA, February 21, 1984. Invited
- G. D. Byrd, "Analysis of a Solid Sludge Material by GC/MS," 35th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 5, 1984.
- F. R. Guenther, "Use of Polynuclear Aromatic Hydrocarbon Generator Columns for Calibrating Air Sampling Systems," 35th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 5, 1984.
- L. R. Hilpert, "Selectivity for Benzo[a]pyrene and Other Polycyclic Aromatic Hydrocarbons Using Negative Ion Chemical Ionization Mass Spectrometry," 35th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 6, 1984.
- M. M. Miller, "GLC Separation Behavior of Polychlorinated Biphenyl Isomers Between a Nematic Liquid Crystal Stationary Phase and a Nonpolar Hydrocarbon Phase (Apolane-87)," 35th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 6, 1984.
- W. F. Kline, "The Use of Perdeuterated PAH as Internal Standards for the HPLC Determination of PAH in Complex Mixtures," 35th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 8, 1984.
- W. E. May, "Organic Analytical Research at the National Bureau of Standards," Department of Chemistry, Hampton Institute, Hampton, VA, March 16, 1984. Invited
- A. J. Fatiadi, "Structure of Metal-Coordinated Polymers: The Chemistry of Oxo- and Pseudo-Oxocarbons," Catholic University, Washington, DC, March 23, 1984. Invited

- W. E. May, "Liquid Chromatographic Methods for the Determination of Polycyclic Aromatic Hydrocarbons and Their Nitrated Derivatives in Environmental Samples," Environmental Chemistry Division, Johns Hopkins University, Baltimore, MD, April 6, 1984. Invited
- G. S. Marbury, "Electrochemical Characterization of a Series of Copper Dithiocarbon Complexes," 187th National Meeting of the American Chemical Society, St. Louis, MO, April 10, 1984.
- S. A. Wise, "Characterization and Quantification of Polycyclic Aromatic Hydrocarbons in Air Particulate Matter from Washington, DC and Philadelphia, PA," Conference and Workshop on Genotoxic Air Pollutants, Rousemont, NC, April 25, 1984. Invited
- S. A. Margolis, "Chromatography," Alice Deal Junior High School, Washington, DC, May 4, 1984. Invited
- E. A. Blubaugh, "Study of 5-Phenyl-2-(4-Pyridinium)Oxazole Methyl Tosylate: Spectroelectrochemistry of a Precipitating System," 165th Meeting of the Electrochemical Society, Cincinnati, OH, May 7, 1984.
- L. C. Sander, "The Influence of Substrate Parameters on Column Selectivity with Alkyl Bonded Phase Sorbents," Eighth International Symposium on Column Liquid Chromatography, May 22, 1984.
- J. M. Brown-Thomas, "Determination of Phenols in Complex Matrices by High-Performance Liquid Chromatography/Electrochemistry," 18th Middle Atlantic Regional Meeting, Newark, NJ, May 23, 1984.
- K. J. Ng, "A Candidate Definitive Method for the Determination of Serum Creatinine by Isotope Dilution/Mass Spectrometry," 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, May 28, 1984.
- G. D. Byrd, "Analysis of a Solid Sludge Material by GC/MS," 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, May 29, 1984.
- L. R. Hilpert, "Measurement of Toxic Organic Compounds in Environmental Samples Using Negative Ion Chemical Ionization Mass Spectrometry," 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, May 29, 1984.
- M. J. Welch, "Photodissociation of Ions Generated by Soft Ionization Techniques," 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, June 1, 1984.
- R. A. Durst, "Analytical Aspects of Chemically Modified Electrodes," 37th Annual Summer Symposium on Analytical Chemistry, NBS, Gaithersburg, MD, June 12, 1984. Invited
- S. A. Wise, "Standard Reference Materials for Urban Air Particulate Matter--Characterization and Uses," Fourth Symposium on Environmental Analytical Chemistry, Brigham Young University, Provo, UT, June 19, 1984. Invited

- R. A. Durst, "Chemically Modified Electrode Sensors," Gordon Research Conference on Synthetic Membranes, New London, NH, June 26, 1984. Invited
- R. A. Durst, "Charge Transport Phenomena in Polymer Film Electrodes," Gordon Research Conference on Synthetic Membranes, New London, NH, June 28, 1984.
- B. Coxon, "Detection and Measurement of the Aldehyde Forms of Aldoses by NMR Spectroscopy," 12th International Carbohydrate Symposium, Utrecht, Holland, July 3, 1984.
- B. Coxon, "Spectrum Editing of the Carbon-13 and Nitrogen-15 NMR Spectra of Carbohydrates by the DEPT Technique," 12th International Carbohydrate Symposium, Utrecht, Holland, July 3, 1984.
- B. Coxon, "Determination of Lactose in Dried Milk by Proton NMR Spectroscopy and by High-Performance Liquid Chromatography," 12th International Carbohydrate Symposium, Utrecht, Holland, July 5, 1984.
- B. Coxon, "Two-Dimensional DEPT Heteronuclear J-Resolved Carbon-13 NMR Spectroscopy of Carbohydrates," 12th International Carbohydrate Symposium, Utrecht, Holland, July 5, 1984.
- J. M. Brown-Thomas, "Chromatography," Satellite '84 Summer Enrichment Program for Gifted and Talented Students, Howard University, Washington, DC, July 16, 1984. Invited
- R. A. Durst, "Thermally Crosslinked Polymer-Film Electrodes," UNESCO-NSF Workshop on Photoelectrochemical Processes and Modified Electrodes, University of California, Santa Cruz, July 23, 1984. Invited
- R. A. Durst, "Charge-Transport Models for Polymer-Film Electrodes," UNESCO-NSF Workshop on Photoelectrochemical Processes and Modified Electrodes, University of California, Santa Cruz, July 24, 1984. Invited
- D. J. Reeder, "Approaches to Standardization in Forensic Electrophoresis," First International Symposium on the Forensic Applications of Electrophoresis, FBI Training Academy, Quantico, VA, July 25, 1984. Invited
- G. S. Marbury, "Electrochemical/Spectroelectrochemical Study of Copper Dithiolene Complexes," Second SUNY Albany Conference on Inorganic and Biochemical Perspectives on Copper Coordination Chemistry, Albany, NY, July 26, 1984. Invited
- D. J. Reeder, "Production and Characterization," Workshop on Standards in Biomass for Energy and Chemicals, NBS, Gaithersburg, MD, August 1, 1984.
- S. A. Wise, "Factors Affecting Selectivity for Reversed-Phase Liquid Chromatographic Separation of Isomeric Polycyclic Aromatic Hydrocarbons on C<sub>18</sub> Stationary Phases," 188th National Meeting of the American Chemical Society, Philadelphia, PA, August 30, 1984. Invited



R. A. Durst, "Chemically Modified Electrode Sensors for Biocomponents,"  
IEEE/EMBS Conference on Frontiers of Engineering and Computing in  
Health Care, Los Angeles, CA, September 16, 1984. Invited

### 3. Committee Assignments

Willie E. May

Chairman, ADABSE, 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

Bruce Coxon

Secretary, ASTM, Committee E13.07 on Nuclear Magnetic Resonance,  
Committee E13 on Molecular Spectroscopy  
Associate Referee, International Commission for Uniform Methods of  
Sugar Analysis, Subcommittee 5 on 100 °S Point of Sugar Scale  
Referee, U.S. National Committee on Sugar Analysis, Subcommittee 5 on  
100 °S Point of Sugar Scale  
Member, Program Committee, 12th International Carbohydrate Symposium

Richard A. Durst

Member, Advisory Board, Analytical Chemistry  
Member, ASTM, Committee D19 on Water  
Member, Board of Advisory Editors, Ion-Selective Electrode Reviews  
Member, Department of the Interior, Office of Water Data Coordination,  
Task Group 5 on Chemical and Physical Quality of Water and  
Sediments  
Member, Instrument Society of America, Subcommittee SP76.02 on  
Electrochemical Analyzers  
Member, IUPAC, Committee V on Analytical Chemistry, Subcommittee 5 on  
Electroanalytical Chemistry  
Member, NCCLS, Subcommittee on Electroanalytical Methods  
Member, NCCLS, Subcommittee on pH and Blood Gases

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, Subcommittee 6 on Quartz Control Plates

Laurence R. Hilpert

Member, ASTM, Committee D34 on Waste Disposal

Dennis J. Reeder

Member, AACC, Committee on Standards  
Study Group on Cortisol  
Study Group on Total Serum Protein  
Associate Member, IFCC, Expert Panel on Drug Effects in Clinical  
Chemistry  
Member, NCCLS, Subcommittee on Total Protein

Robert Schaffer

Member, AACC, Committee on Standards

Subcommittee on Cholesterol

Subcommittee on Creatinine

Subcommittee on Electrolytes

Subcommittee on Glucose

Subcommittee on Iron

Subcommittee on Theophylline

Subcommittee on Urea

Subcommittee on Uric Acid

Member, NCCLS, Area Committee for Clinical Chemistry

Subcommittee on Calibration Reference and Control Materials

Subcommittee on Quantities and Units

Subcommittee on Reference Methods and Materials

Member, Council for National Reference System in Clinical Chemistry

#### 4. Other

##### a. Seminars

- October 12, 1983 - Timothy J. O'Leary, National Institutes of Health, "RAMAN Spectroscopy of Phospholipid Assemblies".
- October 14, 1983 - Thomas McCorkle, LKB Instruments, "Therapeutic Drug Monitoring (TDM) and High-Performance Liquid Chromatography (HPLC)--Past and Future".
- November 10, 1983 - Jeffrey H. Hurst, National Institutes of Health, "Biochemical Studies on Two Catecholamine Synthesizing Enzymes".
- November 10, 1983 - Herbert Pohl, Pohl Cancer Research Laboratory, Oklahoma State University, "Biological Dielectrophoresis".
- December 28, 1983 - Dennis C. Shelley, Indiana University, "Some New Approaches to Environmental Analysis".
- March 9, 1984 - Howard T. Mayfield, University of Alabama, "Pattern Recognition Techniques for Gas Chromatography".
- May 10, 1984 - James L. Meek, St. Elizabeth's Hospital, "Enzymes Adsorbed to an Ion Exchanger as an HPLC Detection Device: Application to Acetylcholine Measurements".
- June 25, 1984 - Robert C. Allen, Medical University of South Carolina, "New Needs for Standardization".
- June 25, 1984 - Bertold J. Radola, Institut fur Lebensmitteltechnologie und Analytische Chemie, "Approaches to Standardization in Isoelectric Focusing".
- July 30, 1984 - Claude Andrieux, Universite de Paris, "Redox Catalysis in Solution and on Modified Electrodes".

- July 31, 1984 - Isiah M. Warner, Emory University, "General Discussion on Multiparameter Luminescence Techniques for Analytical Measurements".
- August 7, 1984 - Isiah M. Warner, Emory University, "Selected Examples and Applications of Multiparameter Luminescence Instrumentation".
- August 14, 1984 - Isiah M. Warner, Emory University, "Qualitative and Quantitative Analysis of Multiparameter Luminescence Data".
- August 16, 1984 - Phillipe Garrigues, Universite de Bordeaux, "Applications of Shpolskii Spectroscopy for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Samples".

b. Conferences Sponsored

- October 23-28, 1983 - W. E. May, Workshop on "A Survey of State-of-the-Art Instrumental Methods for Chemical Analysis," jointly sponsored by the National Bureau of Standards and the Association for the Development and Advancement of Black Scientists and Engineers (ADABSE), National Bureau of Standards, Gaithersburg, MD.
- June 25, 1984 - D. J. Reeder, Workshop on "Electrophoresis Standardization: Approaches and Needs," jointly sponsored by the National Bureau of Standards and the Electrophoresis Society of the Americas, National Bureau of Standards, Gaithersburg, MD.

c. SRM Certification/Information Values

- 1) SRM 41c, Dextrose
- 2) SRM 909, Human Serum
- 3) SRM 1543, Gas Chromatography/Mass Spectrometry Performance Standard
- 4) SRM 1549, Non-Fat Dry Milk
- 5) SRM 1580, Organics in Shale Oil
- 6) SRM 1584, Priority Pollutant Phenols in Methanol
- 7) SRM 1587, Nitro-PAH in Solvent
- 8) SRM 1614, Dioxin in Solvent
- 9) SRM 1650, Organics on Diesel Soot
- 10) SRM 1821a, Ethanol in Water

#### IV. Gas and Particulate Science Division

Harry L. Rook, Chief  
Alan Fried, Deputy Chief

##### A. Division Overview

The Gas and Particulate Science Division conducts research leading to (a) improved analytical methods for quantitative electron, ion, and photon microanalysis; (b) improved quantitative x-ray fluorescence analyses; (c) improved measurements of gaseous species in the atmosphere and in specially prepared gas mixtures; and (d) 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 state and local governments. The Division's programs are carried out by four groups with the research effort divided approximately equally between the two general areas of gas analytical research and microanalytical research.

For the past four years, the Division has been conducting research in compositional mapping with program funds from the Director's Competence Building Program. The goal of this research is to develop quantitative analytical methods for the determination of chemical features on a micrometer spatial scale. This year substantial progress has been made in quantitative compositional mapping, utilizing new capabilities in automated digital image analysis. The system devised for image transfer and analysis for the analytical electron microscope (AEM) was developed in the Microanalysis Research Group to fulfill requirements which could not be met by any commercially available system. Initial testing of the system has demonstrated the capability of transmitting image arrays as large as 512 x 512 pixels derived from any of the image capabilities of the AEM. Image processing software for the system has been developed by Group members which allows the superposition of multiple images such as those from electron and ion beam instruments. Distortions often exist in individual images due to the fundamental characteristics of the optics in each instrument. To overcome this problem, an image processing technique is under development that can automatically recognize comparable features in different images of the same field of view and then correct the distortions to bring individual features of the images into registration. As a result of this research, data from two different instruments with different capabilities can be combined to enhance the ability to calculate elemental or isotopic ratios for a given particle or microscopic feature. In related research, the Cameca IMS-3F ion microscope has been interfaced with a commercially supplied image processing system. Quantitative digital image processing using this system has been evaluated. Some limitations were found in image processing during background subtraction. Correction procedures with the manufacturer-supplied software are being implemented. The results of these research efforts into digital processing of chemical images have brought the Microanalysis Research Group to the scientific forefront of this exciting field.

A second area where major advances have been made is in quantitative isotopic analysis using secondary ion mass spectrometry. Isotopic ratios have been determined with total uncertainties of  $\pm 0.4$  percent relative on submicrogram samples. This level of accuracy is comparable to the definitive

technique of thermal ionization mass spectrometry on bulk samples and expands the applicability of high accuracy isotopic analysis to a host of new samples.

Other significant accomplishments of the past year include: the development of an improved correction procedure for calculating characteristic x-ray fluorescence yields in electron microprobe analysis; advanced research in elemental depth profiling; the development of analytical procedures for organic mass spectrometry using laser ionization; the certification of the first series of glass matrix standards specifically designed for the calibration of electron microprobe instruments; and improvements in the algorithm for calculation of fundamental parameters in quantitative x-ray fluorescence spectrometry.

Research efforts in gas analysis and atmospheric chemistry have focused on two major areas: (a) trace and ultra-trace gas measurements and standards and, (b) the development of a definitive mathematical method for the calculation of lower limits of detection of radionuclides in environmental samples. The results of the latter research, as detailed in a comprehensive document, will be used by the Nuclear Regulatory Commission to revise its regulatory reporting procedures for the detection of radioactive effluents from nuclear power facilities.

Significant progress has been achieved this past year in trace and ultra-trace gas measurement research. A new calibration approach for diode laser spectrometry has been developed and evaluated for measurements of trace levels of HCl. This technique, which utilizes independent calibration based on different molecular concentrations and species, will be expanded to other important atmospheric gases. Along with changes in analytical methodology, instrumental upgrades to the diode laser facility were made this past year to improve measurement capabilities. One example is the addition of a confocal interferometer to allow diode laser linewidth measurements to be carried out simultaneously with absorption measurements, thus assuring accurate quantitative results in cases where the laser and molecular linewidths are comparable.

Research also has been carried out in three new challenging gas measurement areas. The first is a program to develop a calibration system to generate known quantities of tritium at approximately ambient atmospheric levels. This calibration system will be used to put world-wide monitoring data for atmospheric tritium on a common measurement scale. The second research program is the initiation of efforts to develop stable mixtures of reactive gases such as SO<sub>2</sub>, NO, and NO<sub>2</sub> in N<sub>2</sub> at concentrations at or below 1 part-per-billion (ppb). Such standards would be used to provide measurement quality assurance for tropospheric monitoring programs in NASA, EPA, and NOAA. The third program involves measuring the temperature dependence of selected band strengths for the halocarbons F-11 and F-12. These molecules have become increasingly important in model-dependent calculations of atmospheric warming and in calculations of perturbations to the Earth's ozone layer. The effect of temperature on the infrared absorption of these molecules has not been well measured. These data are critical for accurate modeling of atmospheric warming. Moreover, such data are needed for accurate determinations of F-11 and F-12 concentrations throughout the atmosphere, a requisite for accurate modeling of ozone destruction.

An important result of this year's program with other Federal agencies such as NASA and EPA has been to develop a program of measurement traceability whereby estimates of precision and accuracy of a chemical measurement process are obtained and transferred by a system of primary, secondary and working standards. The traceability system has been adopted in principle by the Quality Assurance Division of EPA and the Gas and Particulate Science Division. Traceable standards have been provided for national ozone monitoring and for programs assessing levels of toxic organic gases. The temperature dependent ultraviolet absorption cross-section data obtained for ozone during the past three years is complete and is now ready for distribution. These data have been proposed by NASA to the World Meteorological Organization as the international standard data set for all international ozone monitoring programs. These data form the basis for intercomparison of satellite observations and ozone data derived from the ground level Dobson network.

Other important programs of the past year include: the development of four new ppb level multicomponent gaseous organic compound SRM's and traceable secondary standards; the completion of three new CO<sub>2</sub>-in-Air SRM's with certified values for CO<sub>2</sub>, N<sub>2</sub>O, and information values for CH<sub>4</sub>, F-11 and F-12; the development of a new catalytic methanation system for use in the analysis of CO and CO<sub>2</sub>; continued development of a diode laser spectrometer to study spectroscopic and kinetic properties of reactive atmospheric molecules; and the certification of over 500 individual SRM's.

During the coming year, research efforts in compositional mapping will be expanded to include molecular compositional mapping and complete, three-dimensional mapping using the SIMS system. Other research endeavors planned in the microanalysis group include: extension of image analysis capabilities by applying digital techniques to conventional transmitted electron images and by improved image processing algorithms; further refinements of the isotopic measurement capabilities using ion and laser microprobes; and the development of an advanced laser Raman microprobe with multichannel detection capabilities.

In x-ray fluorescence, development will continue on the fundamental parameter approach to quantitative analysis as well as research in pre-concentration methodology. Research leading to development and certification of new SRM's will also be important activities of this group.

Research in the accurate measurement of, and standards development for, trace and ultra-trace atmospheric constituents will continue to be the lead component of the long-range plans for both the gas metrology and atmospheric chemistry groups. Specific research areas planned for the upcoming year include: continued development of sophisticated lineshape and fitting algorithms for accurate gas concentration measurements using a diode laser; improved measurements of infrared band strengths of selected molecules by FT-IR and diode laser spectroscopy; application of chemometrics to important analytical problems; more accurate measurements of the absolute ozone absorption cross-sections at the wavelengths of several ultraviolet mercury lines; continued development of inorganic and multicomponent toxic organic gas standards; and continued research on the preparation, analysis and stability of ultra-trace gas mixtures.

## 1. Microanalysis Research Group: Overview

The Microanalysis Research Group carries out research to advance the development and application of microbeam analysis techniques for the chemical, crystallographic, and morphologic characterization of matter on the micrometer and sub-micrometer spatial scale. The analytical techniques utilized are based on primary (excitation) particle beams of electrons, ions, or photons, and secondary (analytical) signals of x-rays, inelastically scattered electrons, inelastically scattered photons, and ions. The techniques include electron microprobe analysis, scanning electron microscopy, electron energy loss spectrometry, secondary ion mass spectrometry, and laser microprobe mass analysis. Research on each technique is conducted with the objectives of (1) advancing understanding of the basic physics of sample excitation and attenuation of the secondary radiation; (2) developing methods of quantitation; (3) producing standards and measurement techniques as a means of disseminating developments; (4) developing improved compositional mapping techniques; and (5) applying results of the research to the study of specific analytical problems to support NBS and other government agency missions.

During this past year, advances have been made in each of the major areas of research activities of the Group. In electron beam analysis, the implementation of digital imaging has been accomplished on both the electron probe microanalyzer (EPMA) and the analytical electron microscope (AEM). The system devised for the AEM has been developed as an original hardware/software system by Group members to fulfill a need which could not be met with any system that is commercially available. Initial testing of the system is now underway and has demonstrated its capabilities of transmitting image arrays as large as 512 x 512 pixels derived by scanning transmission electron imaging, scanning secondary electron imaging, scanning electron diffraction, and x-ray area scanning. Important image processing software has been developed which addresses fundamental problems in compositional mapping. A major problem exists when information from different mapping instruments needs to be combined, such as electron beam and ion beam images. Distortions exist in the imaging process of each due to the individual characteristics of their optics. An image processing technique is under development which can automatically recognize comparable features in two images of the same field produced by different techniques and then calculate the corrections which must be applied to bring the images into registration. A second area of image processing development for the AEM concerns the implementation of an algorithm which can accurately characterize linear structures such as those used for magnification calibration.

In the area of ion beam analysis, the Cameca IMS-3F ion microscope has been upgraded by the addition of a primary-beam mass filter. In addition to providing specific selectivity for the variety of ion species produced by the duoplasmatron ion source, the mass filter also permits simultaneous mounting of the cesium ion source. This feature greatly improves the utility of the cesium ion source, which has important applications to problems that cannot be solved using ions derived from the duoplasmatron. Examples of these applications include the analysis of gases in metals, certain species of interest in semiconductors (As in Si, P in GaAs), and detection of carbon. The image processing system of the ion microscope has been used for the study of crystallographic effects in secondary ion emission and to assess the role

of trace elements in modifying the secondary electron emission characteristics of reaction-bonded silicon carbide. Studies of isotopic analysis with the ion microscope have demonstrated its capability of precise and accurate measurements of isotopic ratios with a dynamic range of 100,000 to 1.

In the area of photon beam analysis, the measurement capabilities of the laser microprobe mass analyzer (LAMMA) have been extended to the measurement of isotopic ratios with a dynamic range of 500 to 1. This has been accomplished by developing a correction algorithm to compensate for the non-linearity of the LAMMA detection system. Useful isotopic ratio measurements have been measured for sample masses as small as 0.1 pg, in which accurate values were obtained by making repeated analyses of the same target by the use of grazing incidence excitation. The combination of AEM and LAMMA has been applied to study isotopic distributions within particles of complex mineral systems, such as zircons.

A comprehensive study of instrumentation for laser Raman microanalysis has been completed. This study involved careful comparison of a scanning single channel instrument originally developed at NBS with an advanced multichannel solid state detector instrument developed with NBS collaboration at an Other Agency laboratory. Beam sensitive materials were studied to assess the improvements which could be realized by minimizing the radiation dose to which the sample is subjected during analysis. The improvements in performance were quite pronounced, and the experience gained in implementing the prototype will be used to develop an advanced instrument at NBS.

#### Future Plans:

Future plans in microanalysis research focus on advanced compositional mapping, high accuracy microprobe measurements, and new SRM development. 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. This will greatly extend our analytical capabilities. Image processing algorithms will be developed for direct deconvolution 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.

Ion beam analysis by secondary ion microscopy will be extended to achieve quantitative analyses, both laterally and in-depth, to realize complete three-dimensional compositional mapping. Further refinement of the isotopic measurement capabilities of the ion microscope will be made by the addition of electrostatic peak switching to augment the magnetic peak switching currently in use.

In the area of photon beam analysis, work will begin on the development of an advanced laser Raman microprobe with multichannel detection capabilities and the possibility of molecular compositional imaging. The fundamentals of quantitation of simple molecular mixtures will be investigated.

Dale E. Newbury, Group Leader; Adville A. Bell, David S. Bright, Edgar S. Etz, Robert A. Fletcher, Ryna B. Marinenko, Raymond L. McKenzie, Robert L. Myklebust, Partick J. Sheridan, David S. Simons, John A. Small, Brian R. Stallard, Eric E. Steel, Barbara B. Thorne.



## 2. X-ray Fluorescence Group: Overview

The X-ray Fluorescence Group performs research on: (1) fundamental parameter data reduction methods to increase the accuracy of quantitative analysis of thin and bulk samples; (2) improved sample preparation techniques to increase analytical sensitivity; and (3) development of nondestructive sample preparation techniques for increased analytical speed and reduced cost. A major portion of the work also consists of the quantitative analysis and homogeneity testing of new, and renewal SRM's using a high performance, automated, wavelength-dispersive x-ray spectrometer.

During the past year, we have continued research to improve the accuracy of a fundamental parameter computer program for quantitative x-ray analysis. A significant portion of this program includes the NBS algorithm for calculating the output spectral distributions of x-ray tubes on which we reported last year. Using this program, the results of analysis of several specimen types have been compared with those obtained with another fundamental parameter program, NRLXRF. A research paper on this intercomparison for alloys, pressed powders, and fused specimens is being prepared for publication. Modifications made to the computer program include options for different sample preparation conditions and improved algorithms for calculating mass absorption coefficients.

Several "natural matrix" materials such as clays, ores, and coals were measured to characterize elemental homogeneity and composition leading to the certification of the materials as SRM's.

The laboratory is presently being refurbished to accommodate expanded research efforts in preconcentration sample preparation methods for trace element analysis. These methods focus on the use of thin substrates containing immobilized chelating functional groups that vary in their specificity for different metals. Equipment has been purchased and assembled for performing automated preconcentration of trace elements in such samples as mineral materials and biological samples important to the Standard Reference Material Program.

The fabrication of a limited number of new thin glass films for calibration of x-ray spectrometers has been initiated this year. These films will be used as research materials by the Environmental Protection Agency and will augment the NBS-SRM thin film standards 1832 and 1833 now available.

Upgrading of the energy-dispersive x-ray spectrometer has continued. Acquisition of a high performance desk-top X-ray generator for increased instrument reliability is planned. The recent availability of these compact units has made this upgrade feasible at relatively low cost.

The activities of the X-ray Fluorescence Group for next year will fall into the following categories: (1) evaluation with standard data sets of the fundamental parameter approach to quantitative x-ray analysis; (2) research in preconcentration methodology for increased analytical sensitivity for trace element analysis; (3) characterization of the elemental homogeneity and

composition of new SRM materials leading to their certification as NBS-SRM's; and (4) development of new thin film x-ray SRM's.

Peter A. Pella, Group Leader; Anthony A. Marlow, John R. Sieber, Gerald A. Sleater, Guang-Yi Tao, and Kevin R. Garlow.

### 3. Atmospheric Chemistry Research Group: Overview

The Atmospheric Chemistry Research Group conducts research on measurement techniques for ambient concentrations of atmospheric species in both gas and particle (liquid and solid) phases. This research includes the development of sampling/collection techniques, in situ and laboratory analytical methods, micro-sample preparation and analysis methods, and application of mathematical statistics. A primary objective of this research is the extension of existing, and the development of new, analytical techniques for the detection of trace and ultra-trace level atmospheric constituents.

Research has continued this year on a long term effort to develop and characterize sensitive and selective laser-based spectrometric techniques for the analysis of trace reactive atmospheric gases. Photothermal and tunable infrared diode laser techniques have been used for this purpose. As in the past, significant emphasis has been placed on verifying the accuracy of the trace gas standards employed in these studies. To this end, a new calibration approach, using a known concentration, non-reactive, reference gas, has been assessed successfully and employed in the calibration of a tunable diode laser system for HCl measurements. A computer modeling analysis was developed as part of this procedure to account for response differences between the reactive HCl sample gas and the non-reactive reference gas. This new calibration approach is currently being expanded to include other reactive molecules and presents some significant advantages in cases where known sample gas concentrations cannot be readily generated. Additional progress has been achieved this year in the tunable diode laser research program. Several instrumental upgrades have been added to the existing facility to enhance system versatility and stability as well as the resulting accuracy of quantitative measurements on trace gas species. One such purchase, a confocal interferometer, now allows direct measurement of the diode laser linewidth. With this capability, accurate quantitative absorption measurements can now be carried out in cases where the laser linewidth is a significant fraction of the molecular linewidth under study.

Significant progress has been achieved this past year in the area of environmental carbon research. Techniques have been developed and applied for measuring carbon and carbon isotopes in tropospheric gases and particles. Through the use of Accelerator Mass Spectrometry (AMS),  $^{14}\text{C}$  measurements can now be made on samples containing as little as 50-100  $\mu\text{g}$  of carbon. This represents an improvement of more than a factor of 100 compared to other detection methods and is crucial for a number of atmospheric chemistry studies in which concentrations of climatically significant and toxic carbonaceous species limit the sample size to well below the milligram range. Work completed in this area and carried out jointly with the University of Arizona has provided reliable atmospheric measurements from a variety of sources. This work has also led to a characterization of the overall chemical and isotopic blank in AMS measurements. An additional cooperative study with the Norwegian Institute for Air Research and the Central Institute for Industrial Research has resulted in some very significant conclusions

concerning long-range transport and the nature of local sources. This information is derived from multidimensional patterns among  $^{14}\text{C}$  concentrations in particles, meteorological conditions and the concentration of certain inorganic and organic constituents.

Such multidimensional data interpretation is but one of a number of applications where mathematical and statistical techniques have been applied this past year to analytical data sets. Other important applications of chemometrics include the assessment of detection limits in analytical and nuclear chemistry and the design and improvement of the analytical measurement process. Using these techniques, a two-year study on the lower limit of detection of radiological effluents from nuclear power plant operations has been completed, and a detailed document has been prepared for the Nuclear Regulatory Commission. This document represents the first comprehensive, unified, self-consistent treatment of detection limits for the nuclear utility industry. It provides theoretical background as well as practical guidance for the design and evaluation of nuclear measurements.

In the area of ozone research, final results for the ultraviolet absorption cross-sections in the Hartley and Huggins bands as a function of temperature have been prepared for distribution. Comparisons with other laboratories indicate agreement to within 3% for the absolute values and to within 1% for the relative values. The International Ozone Commission, at its Quadrennial Symposium in September 1984, considered and adopted the NBS results as the standard reference values to be used in the analysis of atmospheric observational data. Collaboration with EPA in their efforts to establish an ozone monitoring network has continued this past year. Additional photometers based on the NBS standard were constructed, and plans are underway to establish a protocol for the regular maintenance and re-certification of the network instruments relative to the NBS primary standard.

The focus of research activities for the next year will include: (a) continued development and application of photoacoustic and tunable diode laser detection techniques for trace and ultra-trace atmospheric gases; (b) development of more sophisticated lineshape and fitting algorithms for accurate diode laser absorption and pressure-broadening coefficient determinations; (c) kinetic measurements of transient species utilizing diode laser spectroscopy; (d) further application of chemometrics in the investigation of problems highlighted in the NRC document, in the study of the design and evaluation of multidimensional data sets, and in the development of simulated numerical data bases for interlaboratory quality assurance; (e) extension of the sensitivity of  $^{14}\text{C}$  detection techniques in environmental samples a few micrograms in size for application to the investigation of sources of atmospheric mutagens; (f) extension of ozone absorption cross-section measurements to longer and shorter wavelengths; and (g) significant improvement in the accuracy of the determination of the absolute ozone absorption cross-sections at several wavelengths of ultra-violet mercury lines using mass spectrometry.

Lloyd A. Currie, Group Leader; Arnold M. Bass, Alan Fried, George A. Klouda, James E. Norris, Jeanne M. Sullivan, and Anne C. Trevey.

#### 4. Gas Metrology Research Group: Overview

The Gas Metrology Research Group conducts fundamental and applied research leading to (a) the improvement of measurements for ambient, trace, and ultra-trace gas analysis, and to (b) the development of accurate and stable standards for the analysis of a wide variety of inorganic gaseous and organic vapor mixtures ranging in concentrations from the percent to the 1 ppb level. Reliable inorganic and organic gas standards are developed to provide data quality assurance in world-wide measurements of gaseous species. Basic analytical research and rigorous measurements are carried out to ensure that the resultant standards are both accurate and stable. Research also is carried out to improve the scientific understanding of causes of chemical instability of gas mixtures, and to more fully characterize spectroscopic and chromatographic detection, and basic properties of gas molecules that may affect accurate gas analysis or the certification of gas standards.

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; provides advice and guidance to the private sector as needed; and addresses gas measurement needs on a world-wide basis. Utilizing its unique capabilities, the Group also performs a limited number of gas analyses for external organizations.

Activities and accomplishments of the Group during the past year include: the development of additional standards to provide data quality assurance in long-term world-wide measurements conducted to quantify changes in global atmospheric CO<sub>2</sub> levels and to assess their possible impact on global temperature and climate; the development of multicomponent, trace organic gas mixtures to provide data quality assurance in national measurements made for toxic, volatile organics in urban and industrialized areas and in hazardous waste incineration operations; the initiation of calibration systems and standards for the quantification of atmospheric tritium levels and the magnitude of other ultra-trace species which contribute to dry acid deposition; the completion of a number of gas SRM's and special gas analyses; the development of several analytical systems for improving gas analysis; and the improvement of computing capabilities for the treatment of analytical data. A brief description of these activities and accomplishments follow.

Three new CO<sub>2</sub>-in-Air SRM's have been completed having nominal certified CO<sub>2</sub> concentrations of 305, 340, and 375 ppm (by mole) and N<sub>2</sub>O concentrations of 270, 300, and 335 ppb (by mole). Representative information values for methane and for F-11 and F-12 halocarbons also are provided for these new standards, making them the most complex atmospheric gas standards developed to date. The first CO<sub>2</sub> concentration data also have been determined in these standards using a new isotope dilution - mass spectrometry technique developed by members of the Inorganic Analytical Research Division. Other CO<sub>2</sub> data have been provided by an independent intercomparison carried out under contract with the Scripps Institution of Oceanography.

A multi-year EPA-sponsored program for the development of NBS-traceable single and multicomponent toxic organic gas mixtures has continued. We accomplished the following: (1) demonstrated one-year stability and accuracy of a 3-12 ppb five-component audit mixture; (2) prepared several special audit mixtures for EPA's use in evaluating the analytical capabilities of contract laboratories; (3) prepared and evaluated several nine-component and

five-component gas mixtures in the low ppb range for EPA's use; (4) developed a special five-component deuterated toxic organic mixture for EPA's use in evaluating uncertainties in blank levels in Tenax traps; (5) prepared and evaluated multicomponent toxic organic mixtures at the one ppb level; (6) prepared standard toxic organic mixtures to assist the development of ID-MS methodology by the Organic Analytical Research Division; and (7) completed the first full set of analyses on the first multicomponent toxic organic SRM's (two SRM's containing benzene, toluene, chlorobenzene, and bromobenzene at nominal concentrations of 10 ppm and 0.25 ppm by mole, respectively). Two technical papers were presented on the preparation of multi-component toxic organic standards, and one technical paper was presented describing the accuracy of the special microgravimetric technique used for preparing these standards.

During the past year, work was initiated in three new challenging areas. One of these has involved the evaluation of a system for the collection and measurement of levels of tritium in the atmosphere and has primarily focused on the development of a stable source of tritium for in situ calibration of the collection system. Accomplishments on this latter activity have included: the design, fabrication, and evaluation of a dynamic dilution system for quantitatively adding tritium to the incoming air stream flowing into the collection system; and the evaluation of potentially stable, accurate sources of tritium, based on the use of a tritium-doped gas cylinder or the use of an electrolytic generating system for hydrogen tritide (HT); and the development of capabilities for low-level tritium measurements using gas proportional counting. Work initiated in the other two areas has focused on research aimed at the development of ultra-trace standards for the reactive gases SO<sub>2</sub> and NO<sub>2</sub> (EPA dry acid deposition studies), and on research to measure the temperature dependence of band strengths for halocarbons Freon-11 and Freon-12 at relevant atmospheric temperatures.

In addition to the above activities, a number of accomplishments have been achieved in our SRM program. These include: the development of new, or the reissuing of existing, gas SRM's; the re-certification of gas SRM's requested by various SRM users; and special analyses.

A total of 61 SRM's received from 12 different SRM users were re-certified, covering the entire range of constituents. Special analyses conducted during the year include: the analysis of binary mixtures of CO, CO<sub>2</sub>, and propane in N<sub>2</sub> for use by the State of California as primary calibration standards for their auto exhaust emission analysis IM program; the analysis of calibration mixtures for the State of Maryland to clarify anomalous results obtained by State auditors at inspection sites in the State's new auto exhaust emission IM program; and the analysis of a variety of gas mixtures for their use as motor vehicle exhaust calibration standards by the Japan Automotive Manufacturers Association. Special analyses also were performed for the U.S. Navy and their Primary Gas Standards Program.

Miscellaneous activities during the past year included: (a) the design and evaluation of a repetitive cryogenic trapping system for the analysis of ultra-trace gases; (b) the redesign and application of a catalytic methanation system for the analysis of CO and CO<sub>2</sub> in air mixtures; (c) the installation of a new computer for the Group's Fourier-Transform IR spectrometer system and its direct coupling to the Division's VAX computer; and (d) the coupling of the Group's computer systems to the NBS net.

Future activities of the Group will involve: (a) the development of CO<sub>2</sub> in air standards at 100 and 1000 ppm to provide wide-range calibrants for measurements of atmospheric CO<sub>2</sub>; (b) continued development in toxic organic standards (including the development of mixtures at 1 ppb, traceable audit mixtures for hazardous waste incineration, completion of two 4-component toxic aliphatic organic mixtures as SRM's, and the addition of GC-MS capabilities); (c) the evaluation of electrochemical methodology (initially, amperometric titration) for the analysis of polar (e.g., SO<sub>2</sub>) gases; (d) an upgrade of the Group's existing gas mass spectrometer; (e) the development of standards for natural gas, certified for total composition and for BTU heating value; and (f) continued research on the preparation, analysis, and stability of ultra-trace gas mixtures.

Two guest scientists have recently joined the Group for one-year appointments: Francois Abbo (from the Center for Research and Development, L'Air Liquide, Paris, France) as a Research Associate interested in the instability of reactive gases (e.g., NO) and in the preparation of stable, ultra-trace mixtures of such gases; and Zhong-tao Cai (from the Shanghai Institute of Ceramics, Shanghai, People's Republic of China) as a Guest Worker interested in the analysis of ultra-trace levels of gases entrained in ceramic materials.

Walter L. Zielinski, Jr., Group Leader; Barry C. Cadoff, William F. Cuthrell, William D. Dorko, James W. Elkins, Ernest E. Hughes, Patricia A. Johnson, Rudolph von Kelly, Gerald D. Mitchell, W. Robert Miller, Richard D. Myers, George C. Rhoderick, and James E. Suddueth.

B. Selected Technical Reports  
(Gas and Particulate Science)

1. Development of an Accurate Calibration Standard for the Measurement of Atmospheric Tritium (15330)

E. E. Hughes and W. R. Miller

Accurate measurement of temporal increases of tritium in the atmosphere can serve as clues to identifying otherwise unpublicized nuclear events of anthropogenic origin. The accuracy of identification depends to a great extent on the accuracy of the individual measurements, which in turn, depends on the reliability of the calibration of the sampling-measuring system currently being used for atmospheric tritium measurements. To address the needs for verifying the reliability of such measurements, a project was initiated earlier this year which focuses on two areas of reliability of the sampling-measuring system, namely, calibration and performance.

Portable calibration systems for the sampling-measuring system are being developed and evaluated, based on the use of a stable source of tritium and a characterized dilution system for coupling the tritium source with the sampling-measuring system. Two approaches to the establishment of a stable tritium source are under investigation: (1) a gravimetrically-prepared gas cylinder mixture of tritium and hydrogen; and (2) an electrolysis cell in which tritiated and normal water will be converted under controlled conditions to a mixture of tritium and hydrogen. The overall reliability of the sampling-measuring system also will be assessed by evaluating its individual components, namely its mechanical pumps, flowmeters, scrubbers (for removing atmospheric water from the sampled air), and the catalytic reaction chambers for converting atmospheric tritium to tritiated water).

Extensive tests with the electrolytic method using a mixture of  $D_2O$  and  $H_2O$  showed a variability of HD generation over a 24-hour period that was similar in magnitude to the variability (2%) in the measurement system (mass spectrometry) being used, indicating that the electrolytic system produces a stable generation rate of HD. In addition, a portable and simple dilution system has been designed, assembled and tested, affording measured concentrations of test gases within 2% of those predicted from the flow rates and the initial concentration of the test gases. This dilution system, coupled with the electrolysis cell, should serve as a useful source of tritium if the results obtained with the dilution system and electrolysis cell are determined to be valid for mixtures of tritium and hydrogen. An apparatus for assessing the capacity and efficiency of the water vapor scrubbers in the sampling-measuring system has been assembled and several tests have been completed. The existence and extent of isotopic discrimination in the system is being studied using hydrogen-deuterium mixtures or mixtures of light and heavy water. Most of these experiments are still in progress.

The successful accomplishment of this research will provide the capability for in situ calibrations of field measurements of atmospheric tritium and a quantitative assessment of changes in its atmospheric concentration.

2. Assessment of Uncertainties in Gravimetrically-Prepared Toxic Organic Gas Mixtures in the Part-Per-Billion Range (15330)

G. C. Rhoderick, W. F. Cuthrell, and W. L. Zielinski, Jr.

A program supported by EPA's Environmental Monitoring Systems Laboratory to develop standards for air pollutants was initiated at NBS several years ago to address a critical need for accurate, stable gas standards for trace levels of volatile, toxic organic species. The establishment of this program was driven by a rapidly-expanding, uncorrelated analytical data base of measurements of such species in the ambient atmosphere. Recently, this program has necessitated the extension of the range of concentrations from the part-per-million level to the intermediate-to-low part-per-billion level. This extension required that modifications be made to the microgravimetric method used for the preparation of part-per-million level standards and that work be undertaken to assess quantitatively the errors associated with the preparation and analysis of standards in the part-per-billion range.

The modified procedure involved a substantial reduction in the size of the sample capillary tubes into which single organics were weighed and subsequently heat-sealed. The overall preparation procedure involved a controlled introduction of the individually-sealed organics into an evacuated and weighed cylinder, pressurizing the cylinder (to 1600 psi or more) with clean, dry, preanalyzed nitrogen, and analysis of the organic analytes in the gas mixture by GC using previously prepared and characterized organic gas mixtures. To assess the preparative and analytical errors associated with the assigned concentration values of the organic analytes, a set of six cylinder mixtures was prepared. The mixtures each contained benzene, vinyl chloride monomer, carbon tetrachloride, chloroform, and tetrachloroethylene, in a nitrogen matrix, ranging in concentration from 3 to 150 ppb. Agreement between gravimetrically-calculated concentrations and concentrations determined by GC analysis against previously-prepared and characterized mixtures of the 5 analytes ranged from 0.5% (for benzene) to 3.6% (for tetrachloroethylene). Separate estimates were made of the individual errors contributing to the overall error of the preparation procedure and to that of the analysis procedure. The total errors for the preparation and analysis procedures were similar in magnitude (ranging from approximately 0.5 - 5%, depending on the organic in question). The two errors were subsequently summed in quadrature to obtain an assigned uncertainty to the concentrations of each of the analytes in each of the six mixtures. The assigned uncertainties (95% confidence limit) ranged from 0.4 ppb for a 24.5 ppb concentration of vinyl chloride monomer (i.e., 1.6%) to 1.6 ppb for a 13.6 ppb concentration of tetrachloroethylene (i.e., 11.8%).

The establishment and relatively low levels of the errors (at 95% confidence) estimated for these low ppb level standards places a statistically-valid margin of accuracy on the concentrations of toxic organic species such that they can be reliably used as traceable standards for the calibration of measurements in field studies conducted nationally. Additional studies have demonstrated that such mixtures have a concentration stability of more than a year.



3. Measurements of the Temperature Dependence of Selected Infrared Band Strengths of Halocarbons F-11 (CCl<sub>2</sub>F) and F-12 (CCl<sub>2</sub>F<sub>2</sub>) (15330)

J. W. Elkins and R. L. Sams

The infrared (IR) properties of the halocarbons F-11 and F-12 have received considerable interest due to their strong IR absorption in the "atmospheric window" region of the electromagnetic spectrum where trace components of the atmosphere are predominant absorbers of re-radiated energy from the earth's surface. Long-term releases of these halocarbons into the atmosphere from anthropogenic activity may increase the earth's global temperature (the so-called "greenhouse effect"). Recent theoretical calculations estimate that the predicted warming effect from an increase in concentration of a few parts per billion (ppb) for both F-11 and F-12 could lead to a "greenhouse effect" which would be approximately 1/3 that predicted by a doubling of the current carbon dioxide concentration (ca. 340 ppm). Both F-11 and F-12 are more effective "greenhouse" absorbers per molecule than carbon dioxide. These halocarbons absorb in a more linear region of Beer's law than CO<sub>2</sub> and away from other interfering IR absorbers in the atmosphere. To adequately describe the warming effect caused by these halocarbons, accurate knowledge of their IR band strengths and band positions is required for theoretical model calculations. Extremely few measurements of these parameters for F-11 and F-12 exist in the literature. Furthermore, most of the band strengths are at low instrumental resolution ( $>0.25 \text{ cm}^{-1}$ ) and at room temperature (296 K). The former can give erroneous values of the band strength.

Climate modelers need to know the band strength at more than one temperature, due to the variations of temperature in the atmosphere. There are three possible empirical relationships for the temperature dependence of the apparent band strength ( $S_y$ ): a square root dependence on the temperature; no dependence; and an inverse dependence. The differences in these relationships and the effect of the temperature dependence on the band strength can be significant. For example, if the atmospheric concentration of F-11 were to increase from the present value of 0.2 to 1 ppb, and F-12 from 0.4 to 3 ppb, the calculated warming effect would vary from +0.42 K (square root dependence) to +0.63 K (inverse dependence). In comparison, doubling the CO<sub>2</sub> concentration to 680 ppm would result in a warming of +2.0 K.

A new research effort recently was initiated to measure the band strengths of both halocarbons F-11 and F-12 using a Fourier Transform Infrared (FT-IR) spectrometer and temperature controlled gas cells at four different temperatures (220, 235, 250, and 273 K), and to reduce the uncertainties of our previous measurements at 296 K. This work is being jointly supported by the Chemical Manufacturers Association (CMA) and NBS. The first phase of this work, which involves the construction of low temperature gas cells, is near completion. A faster mini-computer also has been installed to reduce the computation times for the fast Fourier transforms from 35 min to 6 min and to enhance data analysis. Following completion of the low temperature cell, measurements at the described temperatures will be conducted and compared to literature values where they exist.

4. Development of a Cryogenic Preconcentration Technique for the Analysis of Ultratrace Constituents in Gas Mixtures (15330)

B. C. Cadoff

Preconcentration techniques have been widely used to analyze organic vapors in workplace atmospheres and ambient environments. Such techniques have traditionally used solid or liquid phase sorbents for the concentration of such vapors and are often plagued with errors due to incomplete collection or recoveries of the vapors to and from the sorbents used. Other drawbacks of these techniques have been the absence of clearly-defined precision and accuracy assessments and inadequate assessment of flow rate and volume measurement errors. Cryogenic preconcentration techniques on the other hand, should, in principle, allow for the accurate analysis of organic vapors down to the part-per-trillion level and improve the accuracy and precision of gas analysis at the part-per-billion level.

A gas chromatograph (GC) equipped with a flame-ionization detector was fitted with a gas sampling valve connected to a stream splitting valve which can direct the sample either directly into the GC or into a cryogenically-cooled trap. In one mode of sample introduction, the contents of the gas sampling valve are directly flushed into the GC column. Alternatively, the sample from the gas sampling valve can be directed to the cryo-trap for concentration prior to GC introduction. Evaluations were carried out with samples of benzene in nitrogen at concentrations of 46, 10, and 0.25 ppm. The cryo-trap preconcentrator is a small loop of 1/8-inch stainless-steel tubing, maintained in a bath mixture of dry ice-ethanol. After the sample is collected in the cryo-trap, the loop is isolated from the carrier gas stream and is gently heated in a 30 °C water bath. The vaporized sample concentrate is then connected to the carrier gas stream and flushed into the GC column for analysis.

The results to date indicate that the relative precision of the cryogenic preconcentration method is comparable to the standard method of direct GC analysis within a few tenths of a percent. It was also determined that, when several samples are collected in the cryo-trap, the GC peak areas of composite samples are simple multiples of the peak area obtained from a single sample.

Further work is continuing on the assessment of the precision and accuracy of this method. The system also will be evaluated to assess the accuracy of collecting large samples (100 mL to 1 L or more) so that application can be made to the analysis of gases and vapors at, and below, the ppb level.

5. The Investigation of the Long-Term Stability of Tetrachloroethylene Permeation Tubes (15530)

G. D. Mitchell

The accurate preparation and characterization of stable gas standards are essential for meaningful data quality assurance in the development, evaluation, and practice of analytical methods for gas analysis. In recent years, it has been recognized that a major deficiency exists in the availability of reliable standards for analysis of volatile, hazardous organic

species present at, and below, the part-per-million level in the atmosphere. Such standards are typically provided as compressed gas mixtures in metal cylinders and as liquids in permeation tubes. The latter type of standards complement the former in offering the capability of generating a range of very low concentrations not generally available in compressed gas mixtures in cylinders. Compressed gas mixtures of benzene and tetrachloroethylene have been certified as SRM's, and an SRM permeation tube for benzene also is available. A related project sought to characterize the quantitative performance of permeation tubes containing tetrachloroethylene, an environmentally-important volatile hazardous organic which has been used extensively in the dry-cleaning industry.

Gravimetrically-determined permeation rates of tetrachloroethylene permeation tubes from a common batch have been followed at 25 °C for a period of more than 2.5 years. The permeation rate was observed to gradually increase over the first 16 months of this study, following which, a steady-state rate increase of less than 1% relative per year was attained. Tubes from the same batch that were studied for the first time after 18 months of the study did not show the higher permeation rate increase evidenced by tubes in the first 16 months of the study. These results indicated a long-term stabilization period for the tube material in contact with the permeate. Data also were obtained on a subset of the tubes at 20 and 30 °C; it was observed, however, that a 2-4 week period was necessary before a tube that was carried through such a temperature excursion became re-equilibrated to a stable permeation rate at 25 °C. The data for the full study were examined by linear regression analyses to discern the changes in permeation rate and its stabilization.

The results of this study will serve as the basis for the certification of these tubes as a new tetrachloroethylene SRM. The nominal permeation rate of the tetrachloroethylene is 1 microgram/minute at 25 °C. This SRM will be available for the generation of test atmospheres containing trace levels of tetrachloroethylene and for the calibration of measurement methods used in quantitative analyses of ambient air samples containing this hazardous material.

#### 6. Development of an Improved Methanation System for the Analysis of CO and CO<sub>2</sub> SRM's (15330)

R. C. Myers

A gas methanation system using a Ni catalyst and coupled to a gas chromatograph containing a flame-ionization detector (FID) has been used as one of two possible techniques for the quantitative measurement and certification of CO/N<sub>2</sub>, CO/air, CO<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/air SRM's. The in situ catalytically-produced methane is analyzed by gas chromatography. The Ni catalyst, however, has been found to be susceptible to poisoning by oxygen during analysis of CO and CO<sub>2</sub> in air mixtures.

In the case of CO<sub>2</sub>/air samples, this problem can be resolved by using a palladium catalyst before the Ni catalyst. The palladium catalyst reduces the oxygen to water which has no effect on the Ni methanation catalyst. In the case of CO/air mixtures, however, the palladium catalyst also removes CO. Therefore, a new methanation system using GC separation to remove O<sub>2</sub> followed by a Ni catalyst was designed for the analysis of CO SRM's.

In this new design, an automated in-line 10-port gas sampling valve was installed between the end of the GC column and the Ni catalyst bed. The valve served to inject the sample and vent the eluted oxygen peak, following which it was switched to allow the eluted CO (or CO<sub>2</sub>) peak to enter the Ni catalyst bed, with the resulting methane entering the FID. The valve was time-sequenced through a programmable integrator connected to the GC to also permit repetitive automated sample injections. This mode of operation ensures that each valve switching operation occurs at precisely the same time for each sample. Hence, equal treatment of samples is achieved. Using high-purity carrier and fuel gasses in conjunction with several in-line gas purifiers, the Ni catalyst system has been operated for a period of over 6 months without any significant signs of deterioration.

The development and establishment of this system has provided a reliable, highly-precise analysis method for the certification of CO/air (and CO<sub>2</sub>/air) SRM's.

7. The Development of a System for Analytical Traceability in the State Motor Vehicle Emissions Testing Program (15330)

W. D. Dorko

Many states are implementing motor vehicle emissions testing programs, referred to by the U.S. Environmental Protection Agency as IM (Inspection and Maintenance) programs. Such programs require that motorists take their private vehicles each year to locally-designated testing facilities where the exhaust gases emitted from the vehicle tail pipe are directly tested to determine levels of carbon monoxide, hydrocarbons, and carbon dioxide. Most of the testing is carried out with non-dispersive infrared analyzers (NDIRs), which are not absolute instruments and require periodic calibration. Since the NDIR signal can suffer from interferences from other gases being analyzed, the calibration gases are designed to simulate the auto exhaust for the three gases being measured. To illustrate the magnitude of the measurement problem, the State of California has approximately 7,000 NDIR analyzers that require routine calibration at least once a week. As a quality assurance check, California has established a program to certify gas companies that are able to supply quality calibration gases. The NBS Gas Metrology Group, at the request of the State of California, has provided three sets of analyzed gas standards to enable California to audit gas companies interested in becoming certified. This mechanism allows California and other states to identify quality suppliers of calibration gases, and offers the potential for IM programs conducted by states throughout the U.S. to be tied to the analyzed standards provided by NBS.

The need for quality control in state IM programs was demonstrated this past year in which a state, not requiring calibration gas vendor certification, experienced difficulties in interpreting data that the state IM Quality Assurance group had obtained. This state suspected that its calibration mixtures, obtained by low-cost bidding, were incorrect, and requested NBS assistance. Two cylinders containing a propane calibration gas mixture that were being used for hydrocarbon emission testing and were presumed to have identical propane concentrations (nominally, 2500 ppm propane each) were

supplied by the state in question. Analysis revealed that the propane concentrations in these two cylinders were, in fact, 2600 and 3200 ppm, respectively.

The above experience is probably not unique, and similar inconsistencies will undoubtedly continue to occur until all states adopt a vendor certification program.

We are interested in continuing to interact with IM programs conducted by states and to provide appropriate assistance as requested to aid in the establishment of data quality assurance in state IM programs.

8. Advances in Carbon Isotopic Ratio Measurements by Accelerator Mass Spectrometry (15330)

L. A. Currie, G. A. Klouda, J. M. Sullivan, and W. Ollison

Over the past few years, results of carbon and carbon isotope measurements on tropospheric gases and particles have given important information about sources of carbonaceous species in the atmosphere. The value of carbon isotopic measurements is exemplified by the importance of  $^{14}\text{C}$  as a tracer for carbon from wood-burning which is increasing rapidly. These data have added significance because of (a) the increased emissions of CO and aerosols from wood combustion and (b) the recognition that  $^{14}\text{C}$  is perhaps the only reliable atmospheric tracer for wood-burning generated pollutants. This year's continued progress in trace carbon analytical chemistry focused on the development and validation of techniques for measuring  $^{14}\text{C}$ ,  $^{13}\text{C}$ , and total carbon in small samples of 50 to 1000  $\mu\text{g}$ . This capability is crucial for many atmospheric chemistry studies where concentrations of climatically significant and toxic carbonaceous species limit the sample sizes to well below the mg range.

Principal research has involved thermal separation of elemental ("graphitic") carbon and organic components from source and ambient particles, followed by characterization for  $^{13}\text{C}$  and  $^{14}\text{C}$ . In addition, Urban Particulate SRM's have been assayed for total carbon, carbon in the PAH (Polycyclic Aromatic Hydrocarbons) fraction (cooperatively with B. Diamondstone and S. Wise of Divisions 551 and 552, respectively) and  $^{14}\text{C}$  in each fraction. A dramatic difference in isotopic composition of the two carbonaceous fractions was observed, reflecting a corresponding difference in origin.

The measurement of  $^{14}\text{C}$  itself has been extended from our initial mass range (-5-10 mg carbon) to 100  $\mu\text{g}$  carbon as a result of the use of Accelerator Mass Spectrometry (AMS). The AMS sample preparation at this level has been evaluated, and the overall chemical blank has been determined to be equivalent to 15  $\mu\text{g}$  of contemporary carbon. Work completed in this area was reported at the 3rd international AMS Conference in April, 1984.

This past year we have applied the above techniques to characterize atmospheric methane, as well as carbon particles from a vehicle tunnel, wooded areas, and wood-burning communities. A study completed in cooperation with the Norwegian Institute for Air Research and the Central Institute for Industrial Research in Norway gave interesting correlations among the  $^{14}\text{C}$  concentrations in particles, the meteorological conditions and certain

inorganic and organic constituents. Measurements of  $^{14}\text{C}$  permitted the determination of the winter-time contribution of wood-burning to the carbonaceous particle burden in suburban Oslo. This was found to average about 70%.

Future work with environmental  $^{14}\text{C}$  will focus on extending the sensitivity down to a few  $\mu\text{g-C}$  using advanced sample preparation techniques in which most or all of the chemical steps take place within a single system. This will be linked with exploratory work with physicists at the University of Pennsylvania tandem accelerator laboratory on the direct injection of  $\text{CO}_2$  into the accelerator ion source. Additionally, we have underway studies of carbon isotopes in atmospheric  $\text{CO}$ ,  $\text{CH}_4$ , and volatile organic carbon (the latter in cooperation with a visiting scientist from the American Petroleum Institute), to answer some long standing questions concerning anthropogenic vs natural origins of these species.

9. Development of a Definitive Treatment for the Calculation of Lower Limits of Detection in Radionuclide Monitoring (15330)

L. A. Currie

A monograph has been prepared at the request of the Nuclear Regulatory Commission (NRC) treating all major facets of the problem of estimating the Lower Limit of Detection (LLD) in measurements of effluent and environmental radioactivity. The monograph will serve as a manual for the guidance of contractors, nuclear utilities and the NRC in the calculation of LLDs in connection with Technical Specifications that are required for monitoring effluents from operating nuclear reactors. Prior to the preparation of this manual, the NRC had no single or unified source of guidance on this matter which adequately represented their position.

At the outset of the two-year project which led to this manual, a comprehensive review was made of the literature on detection limits in nuclear and analytical chemistry, spanning a period of 60 years with emphasis on the last two decades. Following this, a number of site visits and meetings took place with representatives of NRC Headquarters and Regional Offices, a trade organization (Atomic Industrial Forum), personnel from nuclear power reactors, a standards laboratory, and commercial contracting (radiochemical) laboratories. These visits confirmed the need for a manual since quite diverse and inconsistent approaches were in use.

The subject manual covers highlights of the current literature as well as the nature of the regulatory requirement. Problems identified are treated comprehensively in two sections: one presenting the basic principles of detection and LLDs using the hypothesis testing framework; the other giving explicit derivations and numerical illustrations for cases confronting the nuclear industry. Topics covered include detection decisions vs detection limits; the basic development in terms of the blank, its standard deviation (variability), and calibration factors; the effect of deviations from normality, as in low-level alpha counting; resolution algorithms and detection in multicomponent spectrometry and decay curve analysis; continuous monitors such as noble gas count rate meters; multiple detection decisions; reporting of "non-detected" results and the impact on averaging; and finally, treatment of bounds for systematic error in the blank, in calibration factors, and in spectroscopic models. Guidance on the design of nuclear

measurement processes to meet prescribed LLDs is also given, together with comments on system optimization and asymptotic limits imposed by systematic error and radioactive decay.

The comprehensive treatment provided by the manual should alleviate many of the divergences in current practice, and it presents for the first time, guidance for NRC licensees for the treatment of complex but realistic problems involving LLDs in Y-ray spectroscopy, ultra-low-level counting, and the inclusion of estimates of systematic error. A number of these topics required new research in order to generate adequate and consistent solutions. The results of these studies will be published separately in the scientific literature.

10. A System for Traceable Calibration of Ozone Measurements Using the NBS Primary Ozone Photometer (15330)

A. M. Bass

We are continuing to work with the Environmental Protection Agency (EPA) on the development of their ozone monitoring network. In this connection we have provided to EPA several photometers based on the NBS primary standard, and additional instruments are being planned.

The EPA has established ultraviolet absorption photometry as the recommended method for the calibration of ozone-monitoring instruments. Based on our experience in photometric measurements, we developed a highly sensitive and accurate instrument to serve as the NBS primary standard for ozone assay. Similar photometers have been assembled at NBS for use by the EPA in their program. These instruments will permit the EPA to maintain a uniform ozone calibration system throughout their regional laboratories.

During the past year two photometers were certified and delivered to EPA, for a total of three instruments delivered. Construction was started on two additional EPA instruments. These are scheduled for delivery by January 1, 1985. The EPA has performed in-house tests of these instruments and has been completely satisfied with them. Planning is underway to establish a protocol for the regular maintenance and recertification of the network instruments relative to the NBS primary standard.

11. Research in Measurement Methodology Using Diode Laser Spectrometry and the Determination of Spectroscopic and Kinetic Data for Reactive Atmospheric Molecules (15330)

A. Fried and R. L. Sams

In our 1983 report, we presented results of a laboratory study utilizing tunable diode laser absorption spectrometry to detect the important atmospheric gas HCl at concentration levels below one ppb. This work, and the studies presented herein, are part of a long term program to develop and characterize sensitive and selective laser-based spectroscopic techniques for measuring concentrations at, and below, the ppb level (ultra-trace level) of such important atmospheric gases. Development of ultra-trace level standards is an additional and parallel aspect of this program. In the previous report, a new calibration approach, using a known concentration of non-reactive reference gas, was briefly described. In the present study, this

diode laser calibration approach has been fully assessed for measurements of HCl. A detailed computer modeling analysis was developed to account for response differences between the reactive sample gas (HCl) and the non-reactive reference gas (CH<sub>4</sub>). The response factor ratios determined from this analysis were in excellent agreement with experimentally determined values. This intercomparison also revealed the optimum experimental regime in which to carry out such calibrations. Because of some very important advantages, the new calibration approach is being expanded to the calibration of other important reactive molecules. Using this technique, the sample and reference gases can be intercompared directly in the same cell, thus eliminating cell pathlength and repositioning errors as well as large signal extrapolations indicative of more conventional optical calibration techniques. Perhaps the most important advantage is that tunable diode laser measurements of reactive radicals can be performed in the field without the need for a calibrated radical generation system. This has obvious significance for diode laser measurements in the atmosphere.

In addition to the particular calibration approach employed, several other factors dictate the overall accuracy with which gas concentrations can be deduced from quantitative diode laser measurements. Assessing these factors for both absolute and relative measurements and improving accuracy are on-going goals of our research program. Presently, the concentration of most atmospheric species can only be determined with an accuracy in the 10-20% range by diode laser spectrometry using the absolute technique of direct absorption. Our aim is to reduce this to below 5% for a number of important molecules. To this end, progress has been achieved during the past year on two fronts. First, we have improved our existing diode laser facility by procuring a number of instrumental up-grades. One such purchase, a confocal interferometer, will now allow us to directly measure diode laser linewidths concurrently with absorption measurements. This is important for accurate concentration determinations in cases where the laser linewidth is a significant fraction of the molecular linewidth under study. Secondly, we have been actively collaborating with the Molecular Spectroscopy Division at NBS to develop sophisticated computer algorithms for line profiles. Such new profiles, which include the effects of collisional-narrowing, are important to achieve accurate concentration determinations below the 10% level for certain molecules.

During the past year, we have also initiated a tunable diode laser research program to determine spectroscopic and kinetic data for the important atmospheric molecule HO<sub>2</sub>. This work is at the beginning stage, and results will be reported next year.

12. Development of an Improved Procedure to Calculate Characteristic X-ray Fluorescence Corrections from an Electron Microprobe (15330)

R. L. Myklebust

In classical quantitative electron probe microanalysis, the matrix correction factors have been separated into four different terms. These terms are normally called the absorption, atomic number, fluorescence, and continuum fluorescence corrections. Most computer programs employed in quantitative analysis use only the first three correction factors. This is satisfactory for most specimens since the effects of the fluorescence due to the continuum are usually insignificant. We have examined the terms in the



characteristic fluorescence correction in an effort to update obsolete parameters and to test the validity of some of the simplifications used in the computational procedure. This effort is part of a long-term program dedicated to the advancement of quantitative analysis techniques for the electron microprobe.

For significant fluorescence to occur, a characteristic x-ray line (element b) in a specimen must be near, and on the high energy side of, the x-ray absorption edge for the measured x-ray line of another element (element a) in the specimen. X-ray fluorescence of element 'a' by x-rays of element 'b' will add x-ray photons from element 'a' to those excited directly by the incident electrons. If this effect is not taken into account, the calculated concentration of element 'a' in the specimen will be greater than the actual concentration.

Historically, a number of different expressions have been used to calculate the fluorescence effect. We compared the two leading expressions for characteristic fluorescence: (1) the full calculation of fluorescence which is incorporated in the NBS matrix correction procedure, COR, and (2) a simplified version developed by Reed which is incorporated in the NBS matrix correction procedure, FRAME. In addition, we compared results using different values for the fluorescence yields. The COR program used tabulated values for fluorescence yields that were available prior to 1972. In the program FRAME, an expression empirically fitted to the data in COR was used. The results from the original programs were compared with results from both programs modified with the more recently determined fluorescence yield values compiled by Bambynek, et al. The fluorescence yields from Bambynek are much higher than all of the previous values used in the FRAME and COR programs and should generate larger fluorescence corrections. Experimental data exhibiting large corrections for characteristic fluorescence were used to test the different procedures. In the cases examined, the results produced by Bambynek's expression show an improvement of 3% relative or better over the previous formulations in both COR and FRAME. This is a significant improvement since in optimum cases the error from quantitative analysis procedures is 2% relative or less. Reed's expression for the fluorescence correction still appears to be quite adequate for K-fluorescence. Further work is required to test the correction for L-fluorescence and the fluorescence yields for L-shells.

13. Development of an Automated Digital Image Acquisition System for Analytical Electron Microscopy (15330)

R. L. Myklebust, E. B. Steel, and A. A. Bell

Efficient data collection from the analytical electron microscope requires the development of digital image acquisition to replace existing analog methods. A PDP 11/23 computer was interfaced to a JEOL 200CX analytical electron microscope for the purpose of producing digital images from the microscope. The scanning coils (bright field and dark field) of the electron microscope are controlled by digital-to-analog converters (DAC's), and the output of the electron detectors on the microscopes are input to the computer via analog-to-digital converters (ADC's). The characteristic x-ray emissions from a specimen may also be imaged through a multichannel analyzer (MCA) and multiple scalars. The scalars are in turn interfaced to the computer via a digital input module. A network link between the PDP 11/23 and a VAX 11/780

is used to transfer the images to the VAX. A Deanza IP8500 image analysis system operating in conjunction with the VAX is used for image manipulation and viewing.

The multichannel analyzer, its computer, the scalers, and the PDP 11/23 system will all soon be replaced by a VAX 11/730 computer and laboratory automation system together with a modular multichannel analyzer. This new MCA is capable of collecting data from several different energy-dispersive detectors at the same time. The VAX 11/730 will take over all of the functions of the rest of the system and will have a direct memory access (DMA) channel to the VAX 11/780 which should shorten the data transfer time by about two orders of magnitude.

The image acquisition software controls the microscope so that either a scanning electron microscope (SEM) image, a scanning transmission electron microscope (STEM) image, or electron energy loss spectrometer (EELS) image can be obtained. Each image consists of 512 x 512 up to 4096 x 4096 pixels at magnifications of 20X to 800,000X and each pixel has a resolution of 8 bits (256 gray levels). For an electron image, the time required to collect the image is about 2 minutes. Due to the small solid angle of collection for the detector and the low x-ray yield of small particles, x-ray images require a much longer acquisition time; therefore, a smaller number of pixels is collected for these images. Up to 4 elements can be collected simultaneously with the current system. In addition to the x-ray images, x-ray line scans can be produced for up to 4 elements superimposed on the electron image of the area in the microscope field. Some early applications of the system have included analyses of air particulates, asbestos, and several other mineral particulates. The new digital imaging capabilities provide the means for rapid intercomparison of images, combining of image and compositional information, and compositional mapping.

14. Comparison of Boron-10 Depth Distributions as Determined by Spreading Resistance, Secondary Ion Mass Spectrometry, and Neutron Depth Profiling (18224)

D. S. Simons, B. R. Stallard, R. G. Downing, R. F. Fleming, and J. R. Ehrstein

Depth profiling of intentional dopants is an important measurement in the semiconductor industry both for process and device modeling and for process control. A comparison study of boron-10 implants into silicon as measured by spreading resistance profiling (SRP), secondary ion mass spectrometry (SIMS), and neutron depth profiling (NDP) has been conducted. The boron implantations were done at several fluences and energies into bare silicon and through several thicknesses of thermally grown oxides. Both as-implanted and thermally annealed wafers were studied. The purpose of this work was to investigate the feasibility of developing a boron-in-silicon depth profiling standard and to compare individual profiling methods.

The following conclusions emerged from this study. Spreading resistance profiling exhibited a discrepancy in the low concentration tails compared with either SIMS or NDP profiles. This discrepancy, which has been observed previously, is attributable to the distinction between free-carrier profiles as measured by SRP and atomic profiles as measured by SIMS and NDP. While SIMS and NDP measure the same type of profile, the physical processes

that occur in the two analytical techniques are completely different, leading to different analytical characteristics. The detection limit of boron by SIMS where the signal is just detectable in a standard counting time was  $10^{15}$  atoms/cc while that of NDP was  $10^{17}$  atoms/cc, and SIMS required a much smaller sample area to achieve this limit of detection. The depth resolution of SIMS was also found to be superior to NDP. On the other hand, NDP is nondestructive while SIMS erodes a small crater in the sample, and NDP can provide a highly accurate measurement of the total implanted boron dose. Unlike SIMS, NDP profiles of boron through  $\text{SiO}_2$ -Si interfaces showed no detectable measurement artifacts in the profile at the interface. It is clear from this study that the choice of proper profiling technique for boron depends on the type of sample and the information desired, and the use of more than one technique is often advantageous.

15. Development of Improved Elemental and Isotopic Measurements of Micrometer Sized Particles by Secondary Ion Mass Spectrometry (18224)

D. S. Simons

The National Bureau of Standards (NBS) organized, and participated in, a blind round-robin analysis of micrometer-sized glass particles by secondary ion mass spectrometry (SIMS). This study is part of an on-going effort of the Microanalysis Research Group to evaluate and to improve the particle analysis capabilities of various microanalytical instruments. The analyses at NBS were carried out using the CAMECA IMS-3F Ion Microanalyzer.

One phase of the study was the determination of the elemental composition of individual glass microchips from a single melt, with diameters ranging from 10 to 25 micrometers. Special transfer optics were used to maximize the ion collection efficiency from the small emission region. Ion energy discrimination was used to minimize the spectral contribution of molecular ions. Thirteen cations were identified in a survey mass scan. The composition was determined by comparing the ion intensities of the elements from the unknown chips with the intensities of the same elements from standard glasses that were ground into chips of the same size range. Measured concentrations were as low as 300 ppm (atom ratio). The accuracy compared to the batch value was within 5% relative for the major components, and within 10-20% for the minor and trace components. One cation, cadmium, was not detected owing to its low concentration and low ionization efficiency. These results for the thirteen cations compare favorably in accuracy with electron microprobe analysis for the major components. The low atomic number elements lithium and boron and the trace components could not be detected with the electron microprobe.

The second phase of the study involved the determination of the isotopic composition of uranium in individual glass microchips containing 5% (by weight) of uranium oxide. The isotopic abundance of U-235 in the unknowns varied from 0.2% to 0.7% with respect to the U-238. The transfer optics were again set to maximize transmission efficiency and the spectrometer was adjusted to obtain flat-topped peaks. The U-235/U-238 instrumental bias factor was determined from chips of the same elemental composition that were known to have the natural isotopic composition of uranium. Typical accuracy of the isotopic ratio determination was better than 0.5% relative, and it was found to be limited only by counting statistics. This accuracy is about a factor of 5 better than the results obtained from an older generation

of ion microprobes. In addition, for the first time it was demonstrated in this study that a SIMS instrument could determine the isotopic abundances of the minor isotopes U-234 and U-236 at levels below 10 ppm with respect to U-238 in individual microparticles.

16. Evaluation of a Digital Image Analysis System for the Secondary Ion Microanalyzer (15330)

D. S. Simons

In an effort to enhance our ion microscopy capabilities, a digital image analysis system has been acquired for dedicated use with the CAMECA Ion Microanalyzer. The system was developed by a subcontractor according to design criteria and performance specifications defined by NBS. It consists of (1) a 2-stage chevron microchannel plate-fluorescent screen image intensifier that replaces the original single-stage assembly in the ion microanalyzer; (2) a newvicon TV camera that views the ion image distribution displayed on the fluorescent screen through a vacuum window; (3) a video digitizer and frame storage unit that digitizes the analog video signal in real time (1/30 s) and stores it in a 512 x 512 pixel array with 8 bits (256 levels) of intensity resolution; and (4) a minicomputer and software package for image manipulation, including contrast enhancement, multiple image registration, intensity line profiling, and image arithmetic such as background image subtraction.

Several major advantages of the digital image analysis system over real-time viewing of the ion image are the capability to sum multiple frames, thereby improving the signal-to-noise ratio, and the ability to view the acquired image without further erosion of the sample. The visual detectability of low-level signals from localized areas was evaluated using the images of 20 x 20 micrometer squares from an aluminum test sample. A series of images was recorded under different conditions of ion flux, exposure time, channel plate gain, and camera black level setting. The following conclusions were drawn: (1) the optimum channel plate gain for best signal-to-background contrast increases as the ion flux decreases; (2) a flux of 40 ions per second over a 20 x 20 micrometer area can be readily distinguished from background in a one second exposure (a flux of 10 ions per second under the same conditions is at the detection limit) and, (3) detectability of low level signals is limited primarily by background pattern noise, and secondarily by random channel plate noise.

Several examples of the value of the digital image analysis system have already been demonstrated. A series of images of the spatial distributions of different elements was collected from the same area of a nickel-based alloy. The major elements nickel, chromium, and iron showed crystallographic contrast in ion emission among different crystallite orientations which is a SIMS artifact that must be understood and compensated for if image intensity variations are to be converted to compositional variations. Numerical division of one image by another on a pixel-by-pixel basis showed quickly and conclusively that the magnitude of the contrast effect was not identical for the three elements. Titanium and niobium were found to be localized in inclusions. An overlay of the two images, each in a different color, showed these elements to be mainly associated in the same inclusions, presumably a mixed Nb-Ti carbide.

17. Automated Object Identification From Digital Images (15330)

David S. Bright

Object identification by computer, despite the need for further research, presents some very real advantages in our microanalysis research program. Because of this, we have embarked on a long term effort to develop algorithms for recognition of simple two dimensional objects in specialized types of images. Computer object identification is currently being employed in three areas: image matching, positron emission tomography (PET) scan analysis, and electron diffraction pattern analysis.

In the area of image matching, images of spheres on a filter were taken with the electron microscope in the transmission mode and in the scattering mode. The scattering mode image is distorted such that a simple superposition of the two images is not possible. An object sorting procedure has been developed which can identify corresponding objects in both images. Once the entire image has been mapped, the image distortion vector field can be determined and used to match pairs taken in the same modes. As a result, images from two different instruments can now be intercompared.

Analysis of positron emission tomography scans of human brain is being performed in collaboration with scientists at NIH. First, the image of the cross section of the brain is divided by the computer into several dozen segments. Algorithms are being developed to identify these segments or group these segments as meaningful objects. This process relies heavily on spatial relationships of the segments as well as the properties of the individual segments. Upon completion of this project, large homologous regions of the brain will be identified without requiring intervention by highly trained specialized personnel. This capability should significantly reduce the analysis time as well as enhance the measurement precision.

In electron diffraction pattern analysis, an algorithm has been developed for the analytical electron microscope. Diffraction patterns of crystalline samples, taken with the analytical electron microscope, sometimes consist of a regular array of spots from one crystal and many randomly spaced spots. Considering the array of spots to be an object, an algorithm has been developed to extract it and any others, one by one, leaving the randomly spaced spots behind. To extract an object, the algorithm searches for a small group of regularly spaced spots, finds a set of basis vectors for that group, and then finds the rest of the spots that can be located by means of the basis vectors.

18. The Detection and Identification of Surface Organic Species by Laser Ionization Mass Spectrometry (15330)

R. A. Fletcher

The analysis of adsorbed and chemisorbed organic species on microstructures, such as small particles and fibers, is difficult without first extracting the species of interest from the substrates. This homogenizes and possibly alters the sample. Laser desorption directly from the surface of a particle or fiber is a unique and potentially valuable way of analyzing these adsorbates and relates to the objective of molecular compositional mapping on small particles and surfaces. The laser microprobe mass analyzer

(LAMMA 500) is a time-of-flight mass spectrometer that uses a 4  $\mu\text{m}$  diameter focused laser beam to desorb and ionize the sample. For organic analysis, the important aspect of the instrument is the availability of a gentle ionization process. This process utilizes low laser energy density conditions ( $< 1 \text{ J/cm}^2$ ) on the sample surface to preserve the molecular structure of many organic species. With increasing laser intensity, more molecular fragmentation occurs which is useful for deriving structural information about the organic species.

We have demonstrated that a monolayer of paranitrobenzoic acid (pNBA) can be desorbed and detected from the surface of silver island films and silver surfaces. In this instance, the LAMMA was able to detect on the order of  $10^9$  molecules of pNBA with minimal fragmentation to the molecular species. In a second set of experiments, pNBA, succinic acid, and dioctyl phthalate (DOP) have been desorbed from two dielectric surfaces - NBS glass spheres and carbon particulates. These materials were placed on the substrate particle surface by aerosolizing either carbon or glass spheres in a 0.001 mol/L alcoholic solution of one of the above compounds. As the alcohol evaporates, a thin coating of the desired organic species is left behind on the particles' surface. The particles are then caught on a grid and analyzed directly by laser ionization mass spectrometry.

The mechanism for desorption and ionization from both types of substrate materials (conductor and dielectric) is thought to be initiated by rapid heating of the substrate which results from absorption of the incident 10 ns pulsed laser radiation. Analyses of asbestos fibers and fly ash particles coated with organic compounds have been reported recently. Surface analysis by laser ionization can be expanded to examine catalytic surfaces and has been utilized to study polymer surfaces. In collaboration with Dr. A. J. Fatiati (Division 552), polymer surfaces are currently being examined. On these polymer surfaces a new immobilized copper chemistry is taking place by means of coordinated metal complexes and ligand formation on polymer beads. The metal coordination is thought to be only on the surface of the polymer bead. Laser ionization mass spectra of the surface show organometal ion fragments which supports the existence of this new metal structure. Laser desorption/ionization mass spectrometry offers a unique way of analyzing organic surface species on microstructures such as small particles and fibers. Monolayer coatings can be examined with  $\sim 1 \mu\text{m}$  spatial resolution. The fundamental processes involved and the extent of applicability are under investigation.

19. Comparison of Multichannel SIT Vidicon and Monochannel Photomultiplier Detection in Micro-Raman Spectroscopy (15330)

E. S. Etz

As part of our long term micro-Raman research program, two types of experimental Raman microprobes have been developed at NBS: (1) a scanning spectrometer system with photomultiplier (PMT)/photon counting detection and (2) a dispersive non-scanning system employing a prototype spectrograph coupled to a multichannel SIT vidicon detector. In the study conducted this past year, these two very different instruments were employed in the analysis and characterization of particles. The performance figures of merit for both instruments have been evaluated for several classes of microparticulate material. The following instrumental comparisons were of principal interest

in these studies: (1) the relative detection sensitivities, (2) the spectral signal-to-noise ratios from weak scatterers, (3) the various tradeoffs between spectral coverage and spectral resolution, and (4) the data acquisition times in cases where the samples were sensitive or unstable to laser irradiation.

These factors were examined in experiments utilizing a classical double monochromator with a cooled PMT detector and a second microprobe employing a developmental triple spectrograph coupled to a cooled 500-channel SIT vidicon with an optical multichannel analyzer. The two micro-Raman systems acquire, process, and read out the spectral data differently as highlighted in this comparison. Spectra of molecular solids -- (inorganics, organics and polymers) have been acquired with both instruments using 514.5 nm excitation. In the multichannel system, this results in a complete spectrum that is readily observable in real time (30 ms) vs scan times on the order of 5-15 min for PMT detection with equivalent spectral coverage. In other measurements, we have examined the weak Raman spectra of highly colored or opaque solids (e.g., metal oxides, carbides) in which the effective laser power density that can be employed is limited by sample modification due to heating. In a third class of materials, certain organic solids (e.g., nitro compounds), time-dependent photodecomposition readily occurs. In general, spectra of such molecules can be obtained only with multichannel detection employing short (typically 1-3 minutes) signal integration times. It is concluded from these studies that spectrographic detection using the multichannel SIT vidicon system is the preferred method for measuring the weak Raman signals of laser-sensitive, labile scattering species. Future research in micro-Raman instrumentation will examine the relative merits of silicon photodiode array vs. SIT vidicon detection.

20. The Certification of New Multielement Glass Standards for Analytical Microprobes (15330)

R. B. Marinenko

As part of our program to produce and certify microanalytical standards, fifteen glasses have been issued as Standard Reference Materials (SRM's) for use in microanalytical techniques such as electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS). These glasses are unique since they provide matrix compositions not previously available in the more-commonly used standards. Because the materials are vitreous solids, they are single phase and can be homogeneous on the micrometer scale. In addition, small amounts of other oxides, or dopants, have been added to the melt without disturbing the microhomogeneity of the major constituents.

The fifteen glasses are divided into five different SRM's (1871-1875), each containing three glasses and each represented by a different matrix. The matrix glass in each SRM is composed only of the two or three major-component oxides while the other two glasses in the SRM have similar matrix compositions with the addition of small amounts (1-2 weight percent) of several dopants. The five different matrices are lead silicate, lead germanate, barium-zinc silicate, aluminum-lithium borate, and aluminum-magnesium phosphate. The dopants include the oxides of zirconium, titanium, cerium, tantalum, iron, nickel, europium, uranium, thorium, and chromium.

Most of the major constituents in the glasses have been analyzed by wet chemistry and EPMA. A few elements were analyzed by optical emission spectrometry or neutron activation analysis. Certification values were determined from the weighted average of the results obtained from two or three methods of analysis. Weighting factors were based on the observed variability of each analytical technique. A few of the major components are being issued with information values until additional analyses have been completed. The dopant oxides were analyzed with EPMA and are issued as information values on the SRM certificates.

The major constituents in the glasses were tested for both micro- and macrohomogeneity. Periodic integrator traces and random sampling techniques were used. For each glass, intercomparisons between specimens as well as within specimens were evaluated using accepted statistical procedures. No evidence of any practical inhomogeneity was found for any of the glasses.

These glass standards are expected to be of significant utility to the microanalysis community. Similar standards have not been available in the past. Not only are the matrix compositions unusual, but also few standards with known low-concentration elements are presently available.

#### 21. The Analysis of Natural Product SRM's by X-Ray Fluorescence (15330)

P. A. Pella and G. A. Sleater

During the past year, homogeneity studies were performed on various natural products by XRF. Samples included in these studies were coal, limestone, clay, and cement. These samples are being proposed as new Standard Reference Materials (SRM's) or as replacements for present SRM's. The ability to conduct analyses on a large number of similar samples with high precision is an attribute that makes x-ray fluorescence (XRF) particularly amenable for homogeneity studies. Also important in this regard is the fact that most analytical samples can be prepared for XRF study without chemical pre-treatment and that the analytical data can be evaluated statistically after measurement.

The analyses were performed using the Philips PW-1400 automated wavelength-dispersive spectrometer. The automated specimen changer attached to this instrument permitted all the specimens to be analyzed in one continuous operation. In 1980, the computer program, HOMOTS, was developed (Paule, Pella, and Tao) and was used to determine the elemental composition homogeneity. This was accomplished using a series of statistical variance tests on the stored intensity data. Homogeneity tests were performed on SRM 679 (Brick Clay), SRM 88b (Dolomitic Limestone), and SRM's 1632a and 1632b (Trace Elements in Coal).

In addition, quantitative analyses were performed on most samples by comparing the measured intensity data with those from standards. Standards were either synthetic standards, made of selected elements in a benign matrix such as fused glass, or comparison standards consisting of SRM specimens of equivalent elemental composition and of similar matrix to the test specimens. Suitable inter-element corrections were made in calculating concentrations from the intensity data. Quantitative analyses were performed for SRM 1880 ("Black Cap" Cement), SRM 1881 ("White Cap" Cement), proposed SRM 679 (Brick Clay), and SRM 88b (Dolomitic Limestone).



22. Improvements in the Algorithm for Calculating Fundamental Parameters in Quantitative X-Ray Fluorescence Analysis (15330)

P. A. Pella and G. Y. Tao

One of the long-term goals of the X-ray Fluorescence Group is to assess and improve interelement correction procedures for quantitative x-ray analysis for a wide variety of sample types. Previously we examined several correction schemes to check for consistency in the results of chemical analysis. These included selected semi-empirical as well as fundamental parameter correction methods. Fundamental parameter methods are particularly attractive in analytical situations where standards of the same type as the analyte specimens are not available. It has been shown with the fundamental parameter program NRLXRF, for example, that reasonable results on the order of  $\pm 5\%$  relative can be obtained in the analysis of major constituents using only the pure elements for calibration. Further improvement necessitates greater accuracy in first principle parameters such as output spectral distributions of x-ray tubes and fluorescence yields. This past year we have evaluated COLA, a comprehensive algorithm which uses correction coefficients calculated from first principles proposed by LaChance. This computer program (NBSGSC) was extensively modified at NBS to include several options for calibration in addition to the NBS algorithm for calculating x-ray tube spectral distributions for seven commonly used x-ray tubes at any desired voltage. Samples chosen for evaluation included well-characterized alloys, SRM cements in the form of pressed pellets, and selected minerals in the form of fused disks. Both pure element as well as 'type' standards were used for calibration, and the results agree usually within  $\pm 2\%$  relative with the known values for major constituents. Further improvements in the NBS algorithm for spectral tube distribution calculations are anticipated by including a modified electron backscatter function. This will take into account that the electron beam is usually at  $45^\circ$  and not at normal incidence to the tube target material in most commercial x-ray tubes. We expect to evaluate these modifications in our algorithm during the coming year.

A research paper describing our intercomparison work with COLA is expected to be ready for publication before the end of 1984. The extended version of the COLA program which we modified at NBS will be ready for publication as an NBS technical publication in 1985.

C. Outputs and Interactions  
(Gas and Particulate Science Division)

1. Publications

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2. Talks
- Bass, A. M., "Status Report on Ultraviolet Ozone Cross Sections," NASA, GSFC, (11/83), University of Reims, France (5/84).
- Bass, A. M., "Calibration of Ozone Monitors," Harvard University, (6/84).
- Bright, D. S., "Computers and Learning," George Washington University, Washington, DC (3/1/84.)
- Bright, D. S., "Image Analysis with LISP Using Spatial Relationships," Santa Barbara Research Corp., Goleta, CA (7/13/84).
- Bright, D. S., "Computer Matching Two Different Images of the Same Particle Fields," Microbeam Analysis Society, Bethlehem, PA (7/18/84).
- Bright, D. S., "Segmentation of PET Brain Images into Anatomically Meaningful Regions," IEEE Computer Society, Arlington, VA (7/24/84).

- Bright, D. S., "Segmentation of PET Brain Images into Anatomically Meaningful Regions, Progress Summary," NIH National Cancer Inst., Bethesda, MD (8/8/84).
- Currie, L. A., "Some Open Problems in Chemometrics: Detection, Regulation, and Multivariate Data," NBS (10/19/83). (Invited)
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- Currie, L. A., "The Use of Carbon Isotopes in Source Apportionment of Organic Species in the Atmosphere," Workshop on Genotoxic Air Pollutants, USEPA, Rougemont, NC (4/26/84). (Invited)
- Currie, L. A., "Introductory Remarks and Session Chairman for Organic Dating," 24th International Archaeometry Symposium, Smithsonian Inst., Washington, DC (5/18/84). (Invited)
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- Currie, L. A., " $^{14}\text{C}$  as a Tracer for Carbonaceous Aerosols: Measurement Techniques, Standards and Applications," 1st International Aerosol Conference, Minneapolis, MN (9/17/84). (Invited)
- Elkins, J. W., "Recent Results on Band Strength Measurements for a Number of Gases," Nicolet FTIR User's Meeting, Nicolet Instruments, Madison, WI (10/5/83).
- Etz, E. S., "Raman Microprobes and Their Use in Chemical Microanalysis," University of California, Davis CA (1/19/84). (Invited)
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- Etz, E. S., "Analytical Characterization of Explosives Particles with a Multichannel Raman Microprobe," 19th Annual Meeting of the MAS, Bethlehem, PA (7/17/84).
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- Fried, A., "Photothermal Spectroscopy," presented at the Society for Applied Spectroscopy, (2/21/84). (Invited)
- Fried, A., "Laser Spectroscopic Techniques for in situ Detection of Trace Atmospheric Gases," Physical Sciences Lab., New Mexico State University (4/6/84). (Invited)
- Klouda, G., "AMS Sample Preparation: Methods for  $^{14}\text{C}$  in 50-1000 Microgram Samples," 3rd International Symposium on Accelerator Mass Spectrometry, Switzerland (4/12/84).
- Marinenko, R. B., "Use and Abuse of Quantitative Wavelength Dispersive X-ray Microanalysis," 19th Annual MAS Meeting, Bethlehem, PA (7/19/84).
- Mitchell, G. D., "Performance Characteristics of Organic and Inorganic Gas Permeation Tubes as an Standard Reference Materials," National Organization of Black Chemists and Chemical Engineers, Houston, TX (4/26/84).
- Mitchell, G. D., "A Theoretical Approach to the Understanding of Permeation Tubes and Other Control Release Devices," Hampton Institute, Hampton, VA (2/15/84).
- Myklebust, R. L., "A Re-Examination of the Characteristic Fluorescence Correction," MAS, Bethlehem, PA (7/19/84).
- Newbury, D. E., "Scanning Electron Microscopy and Microanalysis", NBS Staff Research Series sponsored by the Research Advisory Committee, (12/15/84).
- Newbury, D. E., "Applications of Scanning Electron Microscopy-Discussion," American Society for Metals, Seminar on "Modern Techniques of Microstructural and Surface Analysis," NBS (4/2/84).
- Newbury, D. E., "Secondary Ion Mass Spectrometry," American Society for Metals, Seminar on "Modern Techniques of Microstructural and Surface Analysis," NBS, (4/3/84).
- Newbury, D. E., "Microscopy and Microanalysis of Solid Specimens," MICRO84 Conference sponsored by the Royal Microscopical Society, London (7/11/84).
- Newbury, D. E., "Use of a Monte Carlo Electron Trajectory Simulation for Quantitative Analysis of Thick Films in the Electron Probe Micro-analyzer," MAS, Bethlehem, PA (7/19/84).

- Newbury, D. E., "Specimen Preparation for Electron Beam Analysis," MAS, Bethlehem, PA (7/19/84).
- Newbury, D. E., "Observations on the Calculation of  $k_{AB}$  Factors for Analytical Electron Microscopy," MAS, Bethlehem, PA (7/19/84).
- Pella, P. A., "Preparation of Reference Materials for X-Ray Fluorescence Analysis", ASTM Committee E02 on Emission Spectroscopy, Bal Harbour, FL (10/19/83). (Invited)
- Pella, P. A., "Analysis with Fundamental Parameters Using a NBS Algorithm for Calculation of X-Ra Tube Spectral Distribution," 33rd Denver X-Ray Conference, Denver, CO (8/1/84).
- Rook, H. L., "Traceability Protocols for Commercially Certified Gas Reference Materials," NBS Director's Workshop on Measurement Service Effectiveness (12/7/84).
- Simons, D. S., "Microanalysis Research at NBS," ACS, University of Delaware, Newark, DE (10/19/83).
- Simons, D. S., "Applications of Laser Microprobe Mass Spectrometry in Biological Research," NIH, Research Triangle Park, NC (2/24/84)
- Small, J. A., "The Analysis of Individual Atmospheric Particles Using Advanced Microprobe Techniques," 1984 Johnson Conference, Vermont (7/12/84).
- Small, J. A., "Sample Preparation Techniques for Particles," MAS, Bethlehem, PA (7/17/84).
- Small, J. A., "X-ray Bremsstrahlung Emission from Solid Targets: An Empirical Model," MAS, Bethlehem, PA (7/20/84).
- Steel, E. B., "Ion Sputtered Thin Glass Film Standards for Analytical Electron Microscopy," 4th Analytical Electron Microscope Workshop, Bethlehem, PA (7/20/84).
- Steel, E. B., "Analysis of Submicrometer Particles Using Sequential AEM and LAMMA," MAS, Bethlehem, PA (7/16/84).
- Zielinski, W. L., Jr., Gerald A. Sleater, and George Ulma, "Evaluation of Degree of Sorption in Collection of Trace Organic Vapors on Sorbents," 35th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ (3/84).
- Zielinski, W. L., Jr., William F. Cuthrell, and George C. Rhoderick, "Gas Chromatographic Analysis and Certification of Gravimetrically Prepared Gaseous Toxic Organic Standards in the Low ppm and ppb Range," 20th International Symposium on Advances in Chromatography, New York City, NY (4/84). (Invited)



### 3. Committee Assignments

#### Harry Rook

Chairman, EPA Scientific Review Panel on Quality Assurance  
Chairman, ASTM D-22.03 Sampling and Analysis of Ambient Atmospheres  
Chairman, Office of Water Data Coordination, Committee 5F  
Member, ASTM D-22 Sampling and Analysis of Atmospheres  
Member, ASTM D-22.05 Calibration  
Member, ASTM D-22.07 Precision and Accuracy of Methods

#### David Bright

Member, ASTM E-29 Particle Size Measurement  
Member, ASTM SC.10 Liquid Particle Measurement

#### Lloyd Currie

Member, Intersociety Committee - Methods of Air Sampling and Analysis  
Member, OAC Computer Utilization Committee  
Associate Member, IUPAC Commission on Analytical Nomenclature  
Member, NASA Scientific Advisory Panel on Tropospheric Chemistry

#### William Dorko

Member, American Chemical Society, Washington Section, Board of Managers  
Member, ASTM D-22 Sampling and Analysis of Atmospheres

#### Edgar Etz

Member, ASTM D-22 Methods of Sampling and Analysis of Atmospheres

#### 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 158/WG-2 Transfer Lines and Sampling  
Member, ISO/TC 158/WG-3 Evaluation of the Characteristics of Analysis  
Member, ISO/TC 158/WG-4 Analysis of Natural Gas  
Member, ISO/TC 158/WG-1 Terminology

#### Raymond McKenzie

Member, ASTM D-22 Sampling and Analysis of Atmospheres  
Member, ASTM D-22.03 Monitoring Instrumentation  
Member, ASTM D-22.05 Calibration  
Member, ASTM D-22.07 Precision and Accuracy of Methods  
Member, ASTM E-29 Particle Size Measurement

#### Robert Myklebust

Member, Microbeam Analysis Society  
Member, ASTM E-2 Emission Spectroscopy  
Member, ASTM E-2.04 Standard Reference Materials

#### Dale Newbury

President, Microbeam Analysis Society  
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, Sigma Xi  
Member, Journal of Electron Microscopy Technique, 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  
Member, ASTM D-22.07 Precision and Accuracy of Methods

Walter Zielinski

Member, Interagency Committee on CO<sub>2</sub> 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  
Chairman, Center for Analytical Chemistry Colloquium Committee

4. Other

a. Seminars

December 19, 1983

Dr. William Herget  
Nicolet Analytical Instruments  
"Gas Analysis with Fourier Transform Infrared Spectroscopy"  
(Division Sponsor: J. Elkins)

March 30, 1984

A. Dixon, Thor Instruments  
"Improvements in the Quality and Spatial Resolution of Small Area X-ray Photoelectron Spectroscopy"  
(Division Sponsor: D. Newbury)

April 9, 1984

J. Michael, Lehigh University  
"Application of Analytical Electron Microscopy to Grain Boundary Segregation in Copper-Bismuth Alloys" (Division Sponsor: D. Newbury)

May 15, 1984

Dr. Wilfried Vandercorst  
Bell Northern Research, Canada  
"Profiling with Quadrupole and Magnetic Sector SIMS Instrumentation" (Division Sponsor: D. Newbury)

b. Standard Reference Materials

X-Ray Fluorescence

1173 NI-CR-MO Steel  
C1173 Cast Steel 3  
C1173a Cast Steel 3  
1618 Vanadium and Nickel in Residual Fuel Oil  
1832 Cements  
1880 Portland Cement, Black  
1881 Portland Cement, White  
2683 Sulfur in Coals

Gas Metrology

1626 SO<sub>2</sub> Permeation Tube  
1658a Methane in Air  
1659a Methane in Air  
1660a Methane/Propane in Air  
1661 SO<sub>2</sub> in Nitrogen  
1662 SO<sub>2</sub> in Nitrogen  
1665 Propane in Air  
1665b Propane in Air  
1666 Propane in Air  
1666b Propane in Air  
1667 Propane in Air  
1667b Propane in Air  
1668 Propane in Air  
1668b Propane in Air  
1669 Propane in Air  
1669b Propane in Air  
1677 CO in N<sub>2</sub>  
1678 CO in N<sub>2</sub>  
1679 CO in N<sub>2</sub>  
1680 CO in N<sub>2</sub>  
1681 CO in N<sub>2</sub>  
1683 NO in N<sub>2</sub>  
1684 NO in N<sub>2</sub>  
1685 Nitric Oxide in Nitrogen NO  
1686 Nitric Oxide in Nitrogen NO  
1687 Nitric Oxide in Nitrogen NO  
1693 SO<sub>2</sub> in N<sub>2</sub>  
1693a SO<sub>2</sub> in N<sub>2</sub>  
1694a SO<sub>2</sub> in N<sub>2</sub>  
1809 Tetrachloroethylene in N<sub>2</sub>  
2612 CO in Air  
2613 CO in Air  
2613a CO in Air  
2614 CO in Air  
2614a CO in Air  
2620 CO<sub>2</sub> in N<sub>2</sub>  
2621 CO<sub>2</sub> in N<sub>2</sub>  
2622 CO<sub>2</sub> in N<sub>2</sub>

2625 CO<sub>2</sub> in N<sub>2</sub>  
2626 CO<sub>2</sub> in N<sub>2</sub>  
2627 NO in N<sub>2</sub>  
2628 NO in N<sub>2</sub>  
2629 NO in N<sub>2</sub>  
2637 CO in N<sub>2</sub>  
2638 CO in N<sub>2</sub>

Atmospheric Chemistry

1648 <sup>14</sup>C in Total C and Organic Fractions  
1649 <sup>14</sup>C in Total C and Organic Fractions

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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 1984 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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