NBSIR 82-2620

Annual Report 1982
Center for Analytical Chemistry

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Washington, DC 20234

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Final

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CENTER FOR ANALYTICAL CHEMISTRY

C. W. Reimann, R. A. Velapoldi, and J. K. Taylor, Editors

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U.S. DEPARTMENT OF COMMERCE, **Malcolm Baldrige**, ***Secretary***
NATIONAL BUREAU OF STANDARDS, **Ernest Ambler**, ***Director***

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Curt W. Reimann, 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 standards 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 medical decisions. The Center serves as the National reference laboratory for assuring the reliability of analytical measurements.

The principal means by which the Center serves as a National reference laboratory is through the development and issuance 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 standards 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. Often, 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 proposed standard materials. As it is not reasonable to contemplate the development of standards to deal with every measurement problem, the Center's program must be multifaceted, seeking a variety of avenues to influence the quality of analytical measurements made in the U.S. In addition to the issuance of standards, the Center exerts influence through close contacts with various communities by means of workshops, symposia, and participation in standards committees. Through such contacts, priorities are established for the production of standards and mechanisms are set in place for their effective use.

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

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. One group, the Laser Analytical Chemistry Group, is attached to the Center office. 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 given.

1. Outputs and Interactions

a. Publications

Reimann, C. W., Velapoldi, R. A., and Taylor, J. K., "Technical Activities 1981, Center for Analytical Chemistry", NBSIR 81-2425.

Demas, J. N., Bowman, W. D., Zalewski, E. F., and Velapoldi, R. A., "Determination of the Quantum Yield of the Ferrioxalate Actinometer with Electrically Calibrated Radiometers", J. Phys. Chem. 85, 2766-71 (1981).

Zalewski, E. F., Geist, J., and Velapoldi, R. A., "Correcting Excitation and Emission Spectra: Past Procedures and New Possibiliites". Proceedings of ASTM Conference on "New Directions in Molecular Luminescence", March 1982.

Velapoldi, R. A., White, P. A., May, W. E., and Eberhardt, K. R., "The Spectrofluorimetric Measurement of Polynuclear Aromatic Hydrocarbons in the Aqueous Effluent of Generator Columns". Submitted: Analytical Chemistry.

Taylor, J. K., "Quality Assurance of Chemical Measurements", Anal. Chem. 53, 1588A-1596A (1981).

Taylor, J. K., "The Analytical Chemist", CHEMTECH, p. 285, May (1982).

Crummett, W. B., and Taylor, J. K., "Guidelines for Data Acquisition and Data Qaulity Evaluation in Environmental Chemistry", in "IUPAC Collaborative Interlaboratory Studies in Chemical Analysis", Edited by Egan, H. E., and West, T. S., Pergammon Press, Oxford and New York (1982).

Kratochvil, B. G., and Taylor, J. K., "A Survey of the Recent Literature on Sampling for Chemical Analysis", NBS Tech. Note 1153, January 1982.

Taylor, J. K., "Guidelines for Evaluating the Blank Correction", submitted to ASTM Journal of Environmental Measurements and Applications.

Taylor, J. K., "Validation of Analytical Methods", submitted to ASTM Journal of Environmental Measurement and Applications.

Taylor, J. K., "Reference Materials - How They Are or Should be Used", submitted to ASTM Journal of Environmental Measurement and Applications.

Taylor, J. K., "The Use of Range Control Charts in Analytical Chemistry," submitted to ASTM Journal of Environmental Measurement and Applications.

b. Talks

J. K. Taylor, "Data Acquisition and Data Quality Evaluation in Environmental Chemistry" - American Society for Quality Control, Newark, DEL., December 14, 1981.

Velapoldi, R. A., "Luminescence and Spectrophotometry" NBS/ADABSE Workshop, October 16-17, 1981.

J. K. Taylor, "Quality Assurance Programs", EPA Las Vegas, NV, January 12, 1982.

J. K. Taylor, "The Role of Analytical Chemistry in a Materials Research Laboratory", University of Petroleum and Minerals, Dhahran Saudi Arabia, February 9, 1982.

J. K. Taylor, "Profile of a Modern Analytical Chemistry Laboratory", University of Petroleum and Minerals, Dhahran, Saudi Arabia, February 10, 1982.

Reimann, C. W., "Trace Constitutents in Human Tissue: Reliability of Measurements", National Institute of Child Health and Human Development, March 9, 1982.

Reimann, C. W., "The NBS Specimen Bank Program", College of American Pathologists, Committee on Environmental and Iatrogenic Toxicology, Chicago, Illinois, April 1, 1982.

J. K. Taylor, "Quality Assurance of Chemical Measurements", E. I. DuPont Co., Wilmington, Delaware, April 27, 1982.

J. K. Taylor, "Principles of Quality Assurance", F & DA, Philadelphia, PA, May 17, 1982.

J. K. Taylor, "Controlling the Quality of Chemical Measurements", Ruder Boskovic Institute, Zagreb, Yugoslavia, June 22, 1982.

J. K. Taylor, "Evaluating the Quality of Chemical Data", Ruder Boskovic Institute, Zagreb, Yugoslavia, June 23, 1982.

Velapoldi, R. A., "The Center for Analytical Chemistry" and "Luminescence and Spectrophotometry", Center for Industrial Research - Oslo University, Oslo, Norway, June 3, 1982.

Velapoldi, R. A., "Overview of the Center for Analytical Chemistry - Technical Programs", University of Trondheim, Trondheim, Norway, June 8, 1982.

Reimann, C. W., "Standardization of Health Measurements", Advisory Group on Chemoprevention, National Institutes of Health, July 14, 1982.

J. K. Taylor, "Reference Materials - How They Are or Should Be Used", ASTM C-26 Symposium, Knoxville, TN, August 9, 1982.

Reimann, C. W., "Proposal to Create a Subcommittee on Analytical Chemistry", National Academy of Sciences, Committee on Chemical Sciences, August 17, 1982.

J. K. Taylor, "Validation of Analytical Methods", ACS, Kansas City, MO, September 15, 1982.

J. K. Taylor, "Quality Assurance of Chemical Measurements", ACS Short Course, Philadelphia, PA, September 24-25, 1982.

Reimann, C. W., "Trends Affecting Analytical Laboratories: Problems and Opportunities", LABCON 82, Chicago, Illinois, September 28, 1982.

c. Committee Assignments

Curt W. Reimann
- Member, Regulatory Affairs Committee, American Chemical Society
- Member, Instrumentation Advisory Panel, ANALYTICAL CHEMISTRY
- Co-Chairman, Symposium on Improving the Analytical Chemistry/Regulatory Interface
- Invited Observer, Ad Hoc Subcommittee of the American Chemical Society Joint Board/Council on Science: "Principles to Improve the Utility of Analytical Chemical Data for Public Purposes".
- Member, American Chemical Society Task Force on Scientific Information to Government
- Member, AdHoc Task Force to Design American Chemical Society Study of the Health of the Chemical Sciences
- Member, Analytical Laboratory Managers Association

John K. Taylor
- Member, ISO/TC48, Laboratory Glassware and Related Apparatus
  - ISO/TC48/SC1, Volumetric Glassware
  - ISO/TC146, Air Quality
  - ISO/TC146/SC3, Ambient Measurements
- Chairman, ISO/TC147, Water Quality
- Member, ISO/TC147/SCI/Terminology
  - ISO/TC147/SC2, Chemical, Physical, Biochemical Methods of Analysis
  - ISO.TC147.SC6, Sampling
  - ANSI TAG, ISO/TC147, Water Quality
  - ANSI TAG, ISO/TC172, Optical Instruments
  - ASTM D19, Water

- Chairman, ASTM D19.01,07, International Standards
    - ASTM D19.05, Inorganic Constituents
    - ASTM D19.07, Sediments
    - ASTM D22, Atmospheric Analysis
    - ASTM D22.04, Workplace Atmospheres
- Vice Chairman, ASTM D22.05, Calibration-Precision-Accuracy
- Member ASTM 22.01, Quality Control, Cochairman
    - ASTM D22.09, USTAG to TC 146
    - ASTM E34, Occupational Safety and Health
    - ASTM E36, Criteria for the Evaluation of Testing & Inspection Laboratories
    - 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 80th Anniversary Celebration Committee
    - NBS Advisory Committee, State Measurement Needs Survey

NBS Representative - Interagency Advisory Committee on Water Data

Rance A. Velapoldi

- 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

d. Center Colloquium Series

October 13, 1981 - Dr. Jacques Versieck, Department of Internal Medicine, "Problems in Trace Element Analysis of Human Samples", Ghent, Belgium.

November 12, 1981 - Prof. Alan D. Adler, Western Connecticut, State College, "Scientific Investigation of the Shroud of Turin".

December 9, 1981 - Dr. Kent K. Stewart, U. S. Department of Agriculture, Beltsville, MD., "Flow Injection Analysis; A Useful Tool for Laboratory Automation".

February 10, 1982	Dr. John Kilty, FBI, "Chemistry in the FBI Laboratory".
April 14, 1982	Dr. John Wohlgemuth, Solarex Corp., "Photovoltaics, The Status of Today's Technology and Its Long Term Potential".
May 19, 1982	Frederick Brech, Fisher Scientific Company, "The Application of Science in the Examination of Works of Art".
	Barbara A. Miller, National Gallery of Art, "Using X-Ray Fluorescence Analysis to Investigate Chemical Factors in the Discoloration of Paper".
	Lucia C. Tang, Library of Congress, "Direct Determination of Elements in Conservation Materials By Flameless Atomic Absorption Spectroscopy."
June 9, 1982	J. A. Conkling, Washington College, "Investigation of Pyrotechnic Mixtures by Thermal Analysis".

B. Voluntary Standardization and Quality Assurance

1. Voluntary Standardization

The availability of carefully evaluated methods, standardized by the consensus of knowledgeable analysts is recognized as an essential component of the quality assurance of chemical measurements. Where such methods are closely related to standard reference materials and to appropriate quality assurance programs, a high quality of data is possible. Closely related to this is the requirement for evaluated and standardized analytical data.

Accordingly, the Center has played and continues to play an active role in the voluntary standardization process, both nationally and internationally. More than one-third of the staff engages in some aspect of this activity and leadership is provided in the following important standardization committees and organizations:

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

Altogether the Center is represented on more than one hundred separate committees, and task groups of various standardization organizations. Such activity provides the opportunity for direct transfer of Center technology to a wide range of constituency. The contacts made at meetings of such organizations provide valuable input into the long-range planning of the Center.

A minor but important role also has been played in liaison with several other organizations. These include the International Organization for Legal Metrology, and the NVLAP program for accreditation of testing laboratories. Representation on the Coordinating Council for Recommended Methods, Office of Water Data Coordination, Department of the Interior has been a mutually beneficial activity.

2. Quality Assurance

Quality Assurance of measurements is aimed at obtaining data that is technically sound and legally defensible. The former requires methodology and measurement practices fully adequate for the end use of the data. The latter demands that all aspects of the measurement process must meet the critical test of peer review and of adversarial examination as necessary. The Center's thrust in quality assurance is in two directions - its internal program, and providing assistance to others in their efforts to obtain quality data.

Quality of output has always been the prime objective of the CAC. Its research outputs have always been subject to both internal and external peer review. Its policy for applied measurements has been to follow the craftsman-artisan approach, based on redundancy to minimize errors and bias. Numerical data are not released until fully validated by one or more of the following techniques - confirmation by independent measurements; use of carefully evaluated methodology; peer review of the data.

The formalized quality assurance plan adopted by the Center incorporates the same measurement philosophy. Its chief difference from previous practices is the improvement of documentation. At the same time a new level of review, for quality assurance aspects, is also instituted. The QA plan further emphasizes the role of planning in both research and applied investigations. In particular, quality assurance plans, specific for each investigation - the certification of an SRM is an example - will be developed prior to initiation of work. Other agency sponsored work will be subjected to the same procedure.

Considerable effort has been devoted during the past year to introducing the QA plan to the staff of the Center. This has included holding a series of group discussions on various aspects of quality assurance and the scheduling of several seminars with invited speakers.

The QA plan of the NBS Office of Standard Reference Materials closely parallels that of the CAC. Since the certification of SRM's is a major Center activity, this is an essential requirement. To test the adequacy of both plans, three pilot programs for the certification of SRM's, using the plans, are in progress - one in each of the CAC Divisions. While no difficulties are anticipated, any modifications of either QA plan will be made which appear to be necessary.

The second aspect of the Center's QA activities relates to assistance provided to the technical community. The Quality Assurance Seminars developed on a pilot basis in FY 1981 have been fully implemented during the past year. The Seminars consist of 2-day sessions in which participants look in depth at the measurement process, consider sources of error and quality control procedures, examine the role of reference materials for data quality assessment, and review statistical techniques for evaluating data. The Seminars also schedule workshops with Center personnel for discussion of good measurement practices in selected areas of analytical measurements.

The Seminar Series was announced by a mailing directed to known purchasers of SRM's. The original plan was to hold two seminars of 30 persons each. Because of a large response, this was expanded to 5 seminars with 50 persons in attendance at each. A special textbook was prepared containing the visual materials presented, and also several reprints of NBS papers concerned with quality assurance. Because of its outline nature, the visual materials are not readily understandable to nonattendees and hence are not available for general distribution. However, the reprints are available on request.

In addition to the seminars described above, special seminars of a similar nature were prepared and presented to meetings of the Environmental Protection Agency and the Food and Drug Administration, at the request of these agencies.

In addition to the above, all of the divisions of the Center have provided assistance to the quality assurance efforts of other government agencies during past years. These were concerned with the development of special quality assurance materials and collaborative test materials, including the supervision of collaborative tests. Details are described in the overviews and technical accomplishments of the divisions that provided the services.

A major activity of the undersigned during the past year has been the development of a set of criteria for evaluating the capability of state metrology testing laboratories, and a procedure for certifying them in specified areas of testing competence. A laboratory must demonstrate both general competence as well as competence in specific test area(s) in order to be certified.

The criteria for general competence consist of basic minimum standards for organization, human resources, and facilities and general equipment. The laboratory personnel must demonstrate the attainment of general competence in basic metrological testing practices, as well. In addition, a certified laboratory must have established and implemented a comprehensive measurement quality assurance program.

Laboratories that substantially meet the above general criteria will be certified by the NBS Office of Weights and Measures in one or more of 15 competence areas, as merited. Such certification will be based on demonstration of measurement expertise in the use of recognized test procedures, the availablility of appropriate special equipment, and measurement standards traceable to NBS.

The evaluation of laboratories will be based partly on their own critical self-appraisal according to detailed criteria contained in the plan, and on the judgment of the NBS Office of Weights and Measures on this and other information, including site visits. This certification program will be initiated in calendar year 1983.

John K. Taylor

C. Pilot National Environmental Specimen Bank Program

1. Introduction

Since 1975, the Center for Analytical Chemistry at the National Bureau of Standards (NBS), in conjunction with the U.S. Environmental Protection Agency, has been involved in research directed toward the establishment of a National Environmental Specimen Bank (NESB). In 1979 a pilot NESB program was initiated at NBS to evaluate the feasibility of a national program by providing research and experience in the various aspects of specimen banking (i.e., collection, storage, and analysis of selected environmental specimens). The major goals of this pilot effort are: (1) to develop protocols for sample collection and storage of four types of environmental accumulators; (2) to evaluate and improve analytical methods for the determination of both trace element and organic pollutants in these biological matrices; (3) to evaluate long-term storage at various conditions; and (4) to provide a "bank" of valid samples for retrospective analyses in future years.

Since 1980, human liver specimens (the first sample type of the pilot program) have been collected, stored, and analyzed. The development of the sample collection and storage protocol and the implementation of the analytical methodologies for the trace element determinations have been summarized in previous reports [1,2]. During the past year the following tasks were accomplished: (1) evaluation of the trace element data for 36 livers collected during the first year; (2) completion of liver sample collection and processing for the second year samples; (3) improvements in the development and application of the cryogenic homogenization technique for biological samples; (4) preliminary evaluation of storage conditions after one year storage; (5) improvements in analytical methods for Cr, Sn, and Pt; (6) initiation of second year liver analyses for trace elements; (7) implementation of methods for determination of organochlorine pesticide residues in livers; and (8) initiation of collection of a second sample type, mussels.

2. Research in Cryogenic Homogenization Techniques

NBS has developed and evaluated the use of Teflon disk mills for the cryogenic homogenization of soft tissues. The initial performance evaluation for a Teflon mill with a 100 g capacity demonstrated the value of this technique. During the past year disk mills with larger capacities (200 g and 1000 g) have been designed and fabricated. For the homogenization of liver specimens, a mill with a capacity of ∼200 g was constructed. This mill (with a total volume of 2500 cm^3) can be modified by inserting one large disk and ring or a smaller disk and two rings; the capacity is 200 g or 300 g, respectively. This design flexibility is necessary because the mills require a minimum filling of 50 percent of the capacity to achieve optimum performance. For homogenization of the mussel samples, a mill with a capacity of 1000 g has been constructed and the performance evaluated. This larger mill has a total volume of 6500 cm^3 and contains one disk and three rings. The performance of the mills can be rapidly evaluated by sieving the frozen tissue powder after homogenization. Two different tissue types have been used to evaluate the performance of the mills: beef liver to simulate the behavior of the NESB human liver specimens and pork belly fat to simulate human adipose tissue.

After four minutes of cryogenic grinding, the homogenates were sieved at cryogenic temperatures in a set of 40 to 200 mesh sieves. The results of these experiments are shown in figure 1. The beef liver homogenate completely passes a 40 mesh sieve and shows a distinct distribution among the sieves. Most of the fat passes even a 100 mesh sieve, however, a small amount of coarse material is left on the 40 mesh sieve probably because of caking due to temperature increase during the milling procedure. For this type of tissue (i.e., fat) temperatures during grinding must be maintained as close as possible to the liquid nitrogen (LN_2) temperature.

3. Analytical Results

The results of the determination of 31 trace elements in 36 liver specimens were reported previously [1]. An interesting result of this study is the very narrow range of concentration data for many essential trace elements (figure 2) as compared to the wide scatter of pollutant element concentrations (figure 3). For example, the concentrations of Se vary by only a factor of 1.8 and other essential elements (Mg, Co, Cu, and Zn) vary by only a factor of 2-3.5, whereas several pollutant elements (Al, As, Cd, Hg, Pb, and Tl) vary by as much as a factor of 100. When compared to the literature data of the trace element content of human tissues compiled by Iyengar (3) (solid lines in figures 2 and 3), the elemental concentrations found in these liver samples, in particular for the pollutant elements, are generally at the lower side of the previously reported data.

Some interesting findings can be pointed out to illustrate the potential utility of a specimen banking program in relation to monitoring environmental trends. For example, the range of Se data is much lower if individuals from the same geographical location are compared. Evaluation of the data by the NBS Statistical Engineering Division revealed a statistically significant difference in average Se values for samples from Baltimore (0.44 µg/g) compared to Minneapolis (0.51 µg/g) and Seattle (0.56 µg/g). Similar evaluations indicated that possible geographic differences may exist for several other elements. The trace element data were also evaluated with respect to possible correlations of variables such as age and sex with elemental concentration and correlations of different elements with each other. Because of the relatively small data set, the results were only partially successful in suggesting some possible correlations. However, as real-time analyses provide additional data in each year of the pilot program, the potential for substantiating these possible correlations will increase significantly.

During the past year, recently developed activation analysis procedures were utilized for the determination of Cr, Pt, and Sn. The newly installed Compton Suppressor system lowers the limit of detection for Cr and Pt. Cr can now be detected at 5 ng/g and Pt at 2 pg/g. With this improved sensitivity the instrumental determination of Cr at the lowest previously reported levels will be possible. In ten liver specimens, which have been banked for one year, Cr was measured at between 9 ng/g and 40 ng/g. This procedure will be applied to provide baseline levels for Cr from the second year sample collection. Pt was determined in 13 specimens of the first year collection and found to range from 5 to 57 pg/g. The application of the radiochemical procedure for Sn on ten specimens gave results of between 0.16 and 0.71 µg/g. The analytical protocol for the second year analysis will reflect these

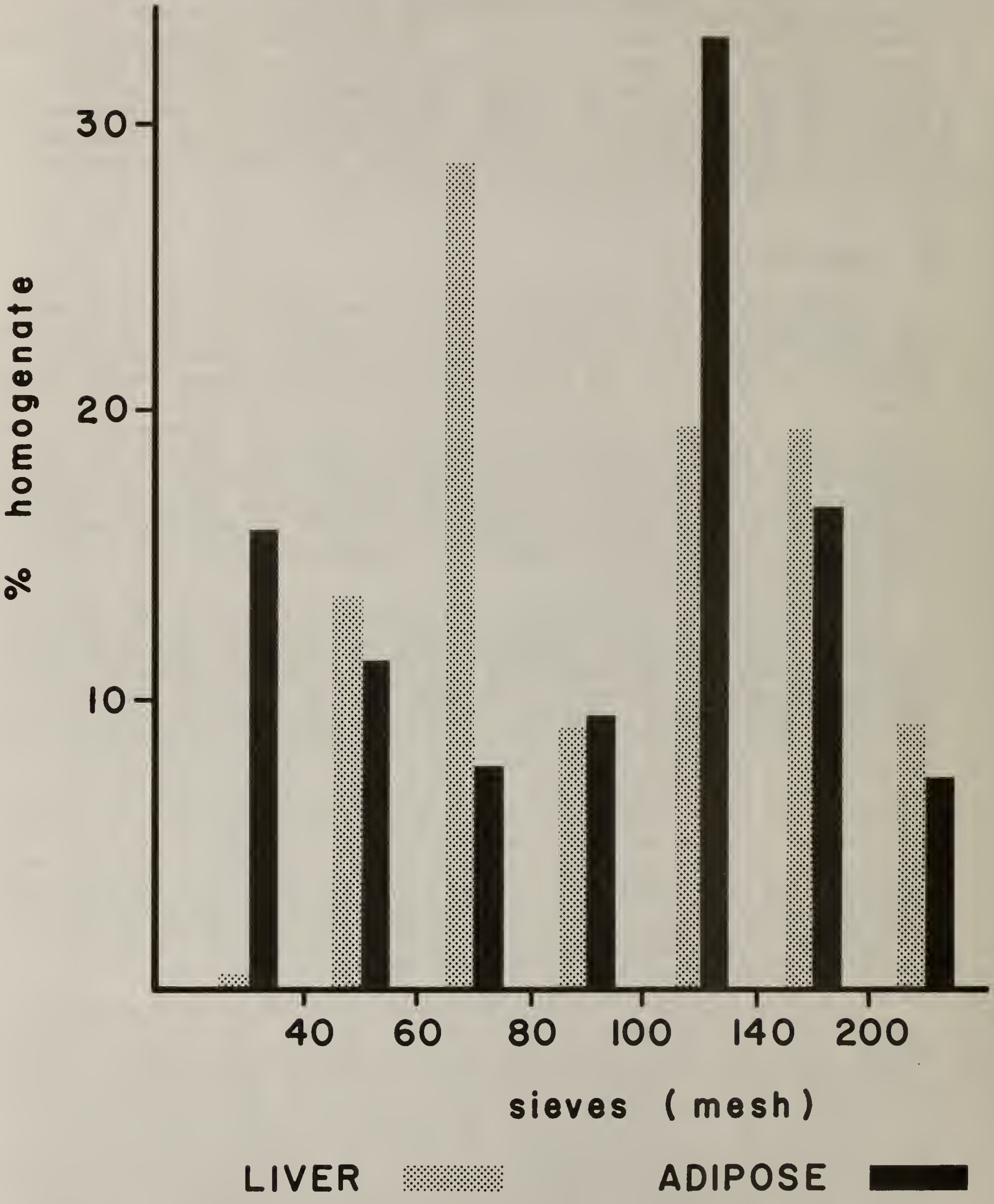


Figure 1. Size fractions of beef liver and pork fat from cryogenic homogenization.

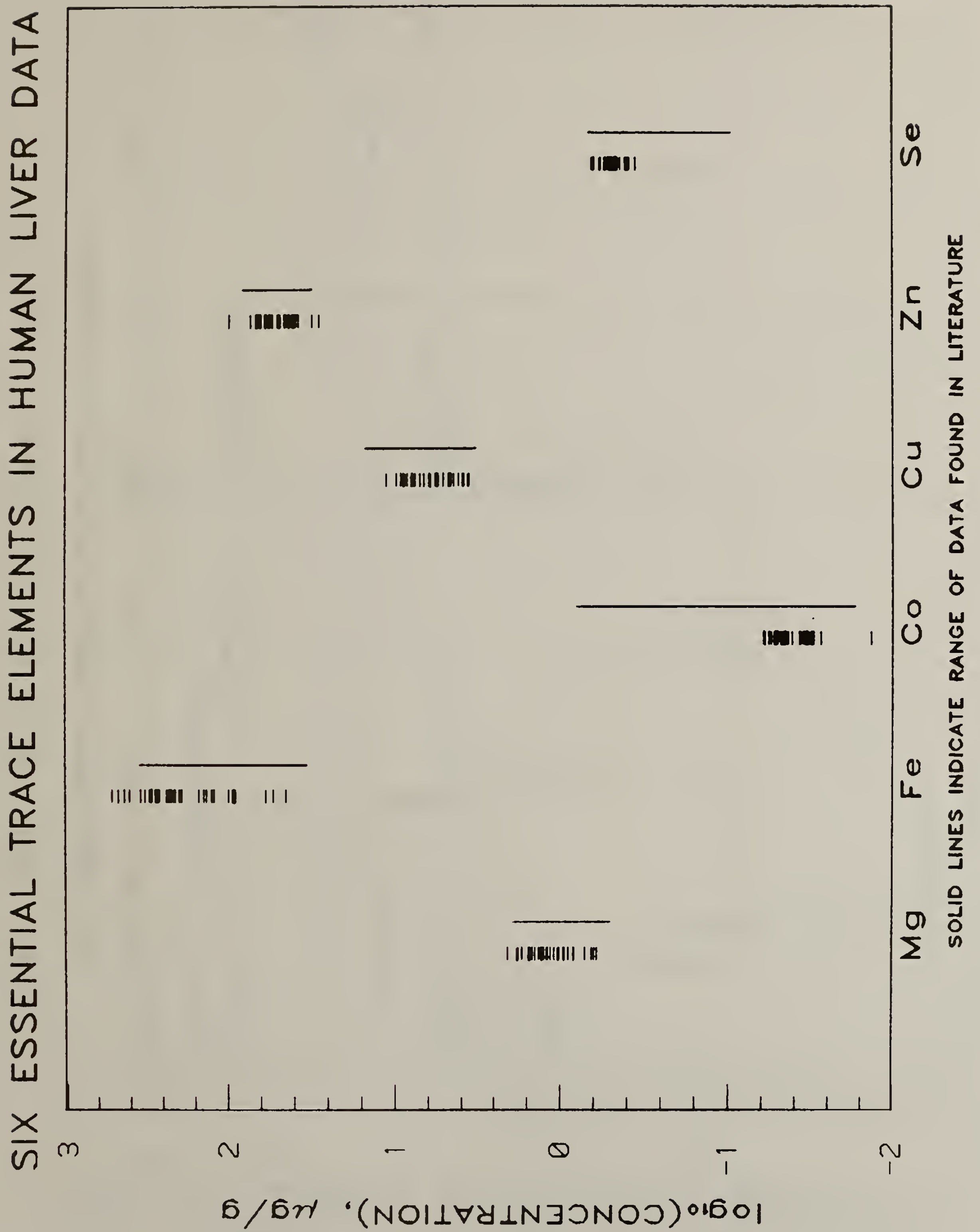
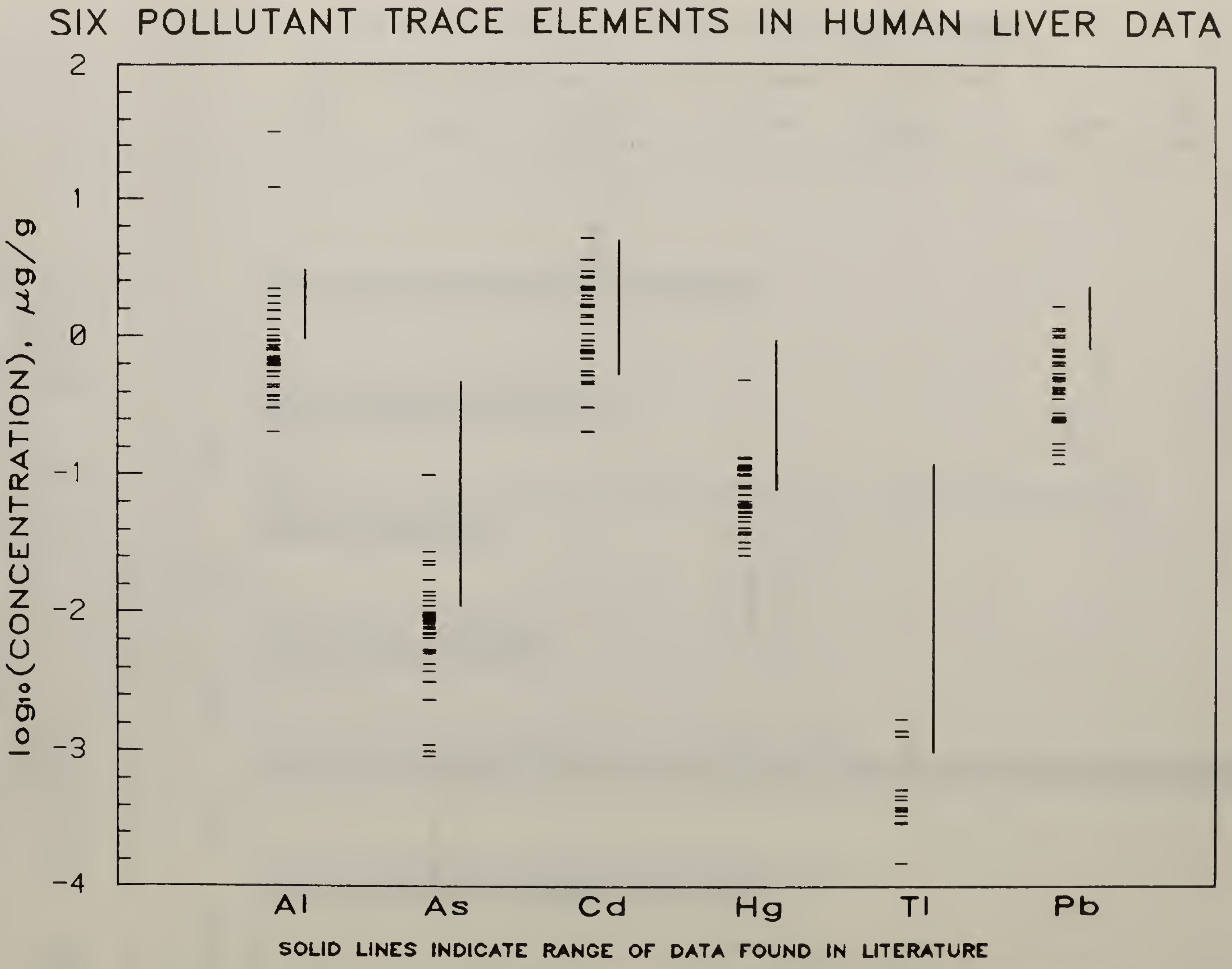


Figure 2. Data for six essential trace elements in human liver.



Fgure 3. Data for six pollutant trace elements in human liver.

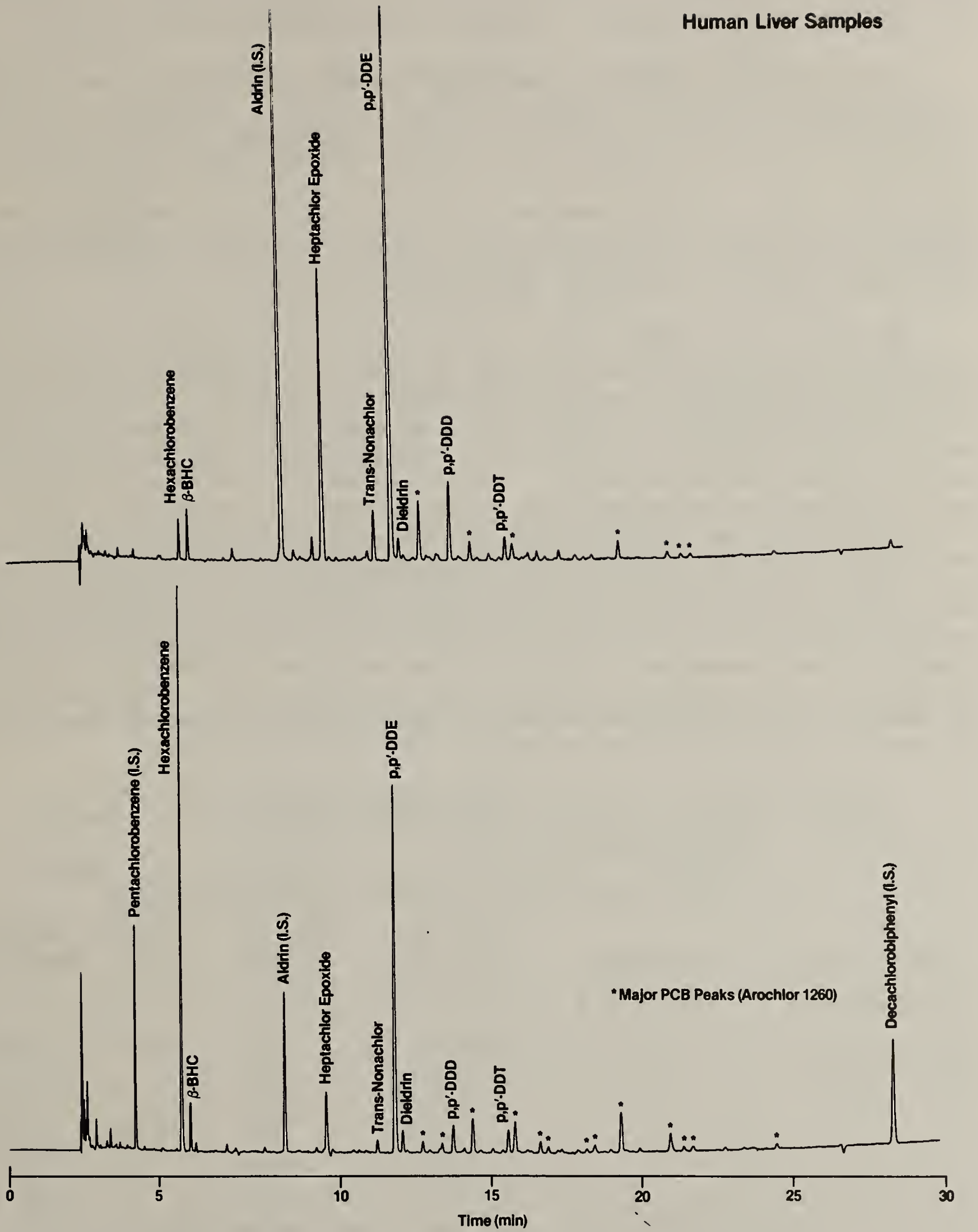


Figure 4. Gas chromatograms from the analysis of human liver samples. (A) Liver sample from NBS/EPA Pilot Program, (B) Liver homogenate from German Pilot Environmental Specimen Bank Program.

improvements in sensitivity for the activation analysis procedures and will also include the radiochemical procedure for the determination of Sn.

A new list of elements to be measured by atomic absorption spectroscopy (AAS) includes Al, Cr, Ni, Cu, As, Se, Cd, Hg, and Pb. The results from AAS will complement the neutron activation analysis data and provide quality assurance on selected elements determined by both methods (i.e., Al, Cr, Cu, Se, Cd, and Hg). Selected samples will also be analyzed by isotope dilution mass spectrometry for determination of Pb, Tl, and Cu. In addition, a fourth independent technique, differential pulse anodic stripping voltammetry, will be applied by the Institute for Applied Physical Chemistry, KFA Jülich, in the Federal Republic of Germany to determine Pb and Cd.

As part of the storage evaluation study, the liver samples were investigated for moisture loss after one year storage. The samples were removed from storage and weighed; the results are summarized in Table 1. The weights of the whole specimens have an estimated uncertainty of about 1 percent or more owing to the inaccuracy of autopsy room equipment and differing weights of packaging and labeling materials. For the subsamples, where we have much better control over weighing errors, some interesting trends were observed. The freeze-dried samples all showed a slight gain in weight which is not surprising since the room temperature storage cabinet is not desiccated. On the other hand, all samples stored at -25 °C showed a slight dehydration. Visual inspection of the subsamples stored at -25 °C revealed water crystals on the inside of the Teflon container and lid indicating a separation of water from the liver homogenate. This separation would make subsampling of test portions from the sample impossible. The first results from the reanalysis of samples for determination of trace elements after one year storage revealed no significant change in concentrations.

Table 1. Weight of Specimen Bank Samples After One Year Storage and Freeze-Drying.

A. Weight Change with Different Storage Conditions

Sample Type	Sample Wt.	Storage Condition	No. of Samples	% Wt. Change	Standard Deviation
Liver specimen	110 - 200 g	≤ -120 °C		<1	
Liver subsample	5 - 9 g	Freeze-dried	19	+0.7	0.23
		- 25 °C	23	-0.23	0.13
		- 80 °C	24	-0.1	0.13
		≤ -120 °C	33	-0.03	0.13

B. Variations in Water Loss After Freeze-Drying

1.	Dry wt/fresh wt for different livers	Range = 0.206 - 0.306
2.	Relative difference in factors between subsamples of the same liver	≤ ±1.5%

Analytical methodology for the determination of organochlorine pesticide residues in human liver has been developed and the analyses of 30 samples from the second year collection are now in progress. A typical gas chromatogram from the analysis of one of the liver samples is shown in figure 4A. The following organochlorine compounds, which are present in most human liver samples, are currently measured: hexachlorobenzene, β-isomer of hexachlorocyclohexane (β-BHC), heptachlor epoxide, trans-nonachlor, p,p'-DDE, dieldrin, p,p'-DDD, and p,p'-DDT.

A sample of a human liver homogenate from the German Pilot Environmental Specimen Bank was analyzed as part of an interlaboratory comparison of methods. The gas chromatogram from the analysis of the German liver homogenate is shown in figure 4B and the quantitative results are summarized in Table 2. The quantitative results from the analysis of a liver sample from the NBS pilot program are also given in Table 1 for comparison. Of particular interest in comparing the two samples is the large quantity of hexachlorobenzene present in the German sample as compared to the U.S. sample. In addition, when quantitation is on an extractable fat basis, the U.S. sample is higher in concentrations of several compounds.

The gas chromatograms shown in figure 4 contain aldrin, pentachlorobenzene, and/or decachlorobiphenyl as internal standards for quantitation. Recent results indicate that quantitation based on aldrin provides more reproducible results than pentachlorobenzene or decachlorobiphenyl. In addition, aldrin is rarely found in biological samples since it is readily converted to dieldrin.

Table 2. Concentrations of Selected Organochlorine Pesticide Residues in Human Livers Samples[a].

	German Homogenate[b]		U.S. Sample[c]	
Compound	ng/g (wet weight)	ng/g extractable fat	ng/g (wet weight)	ng/g extractable fat
Hexachlorobenzene	413 ± 20	3110 ± 260	8 ± 3	190 ± 66
α-BHC	---	---	0.9 ± 0.1	23 ± 2
β-BHC	88 ± 9	670 ± 120	44 ± 12	1100 ± 330
Trans-nonachlor	8 ± 1	60 ± 15	27 ± 6	670 ± 170
p,p'-DDE	305 ± 9	2310 ± 315	195 ± 59	4840 ± 1590
Dieldrin	22 ± 4	170 ± 40	83 ± 38	2030 ± 960
p,p'-DDD	34 ± 5	260 ± 60	---	---
p,p'-DDT	25 ± 5	190 ± 40	25 ± 6	606 ± 163

---

[a] Measurements based on three samples, uncertainty is ±1σ calculated standard deviation based on 2 degrees of freedom.

[b] 13% average extractable fat.

[c] 4% average extractable fat.

4. Second Specimen Type - Mussels

The second sample type for incorporation into the NBS pilot program is marine mussels (Mytilus edulis). A sampling/storage protocol has been developed in cooperation with investigators familiar with mussel collection, i.e., the U.S. EPA Mussel Watch Program. Mussel samples for the NBS pilot bank will be collected from four sites, i.e., two on the Northeastern coast and two on the Western coast of the U.S. Sites with relatively low and high levels of pollutants such as heavy metals and hydrocarbons will be selected on each coast. These sampling sites will be selected in cooperation with the EPA and will correspond to present sites for the EPA Mussel Watch Program. As in the case of the human liver sample collection, the sampling protocol was designed to avoid contamination by metals and organic compounds. Mussels are closed at collection and, therefore, provide some natural protection against contamination during sampling. However, special precautions are followed to minimize the possibility of contamination during sampling, i.e., avoid contact of mussels with metal, uncovered hands, plastics, creosoted pilings, etc. The mussels are thoroughly rinsed and scrubbed to remove debris, sediment, and other foreign material and shipped frozen (dry ice) to NBS. At NBS the samples will be sealed in Teflon bags and stored under various conditions. If mussels are to be stored without shells (or as a homogenate), the shells are removed as soon as possible at NBS under clean room conditions using a special titanium tool (to limit trace metal contamination to only one metal).

The development of sampling, processing, and storage protocols for the second specimen type, mussels, offered somewhat different problems and required the addressing of different questions than those for human livers. For example, the following questions were considered:

- How many mussels constitute a sample?
- What is the expected variability among "pools" of 70-100 mussels from the same site?
- Should the mussels be stored in the shell, shucked (whole), or as homogenates?

The mussel sampling and storage evaluation strategies for the NBS pilot program were designed, in cooperation with NBS statisticians, to address these questions. Initially, samples will be collected at one site to determine the "variability" of these "pools" of mussels. These data will then be used to evaluate the probablity of detecting changes during the storage of the mussel samples under various conditions.

The storage evaluation scheme will be based on the comparison of samples (batches or pools of 70-100 mussels) stored as homogenates, whole (in shells), and whole (without shells). A number of batches (∿15) will be homogenized and analyzed immediately after collection to determine batch-to-batch variability. Subsamples from the mussel sample homogenate will be stored in Teflon jars. Other batches of mussels will be stored whole (in shells) and whole (without shells) in Teflon bags. The whole mussel and the mussel homogenate samples will be stored under various conditions and reanalyzed after one to three years storage for comparison with the analyses performed prior to storage. Mussels from the first site will be collected in October, 1982.

5. Storage of Biological/Environmental SRM's

A major task of the NBS pilot program is the evaluation of long-term storage of biological specimens to assess chemical and/or biodegradation effects on the organic and inorganic constituents. An important aspect of a specimen banking activity should also be the inclusion of biological Standard Reference Materials (SRM's) for comparison. The biological/environmental SRM's listed in Table 3 have been selected for storage in the NBS pilot specimen bank facility. Four of these certified materials, i.e., bovine liver, oyster tissue, wheat flour, and air particulate matter, are matrices representative of the four specimen types to be studied in the pilot program. Several units of each SRM will be stored in the LN_2 vapor freezers and at room temperature. Selected SRM's will be analyzed at various time intervals during the storage evaluation.

Table 3. Biological/Environmental SRM's for Environmental Specimen Banking.

SRM No.	Description	Constituents Certified
1566	Oyster Tissue	Trace elements
1567	Wheat Flour	Trace elements
1575	Citrus Leaves	Trace elements
1577B	Bovine Liver	Trace elements
1580	Shale Oil	Organics (PAH, phenols, and N-heterocyclics)
1633	Coal Fly Ash	Trace elements
1645	River Sediment	Trace elements
1646	Estuarine Sediment	Trace elements
1647	Priority Pollutant PAH (in acetonitrile)	Organics (PAH)
1648	Urban Particulate Matter	Trace elements
1649	Urban Dust/Organics	Organics (PAH)

6. Interactions with National and International Programs

In May 1982, NBS representatives participated in the "International Workshop on Environmental Specimen Banking and Monitoring as Related to Banking" in Saarbrucken, Germany and the "7th Annual U.S./German Seminar of State and Planning on Environmental Specimen Banking" in Munich, Germany. These meetings provided for exchange of information related to research and operational experience in environmental specimen banking. At present, the pilot specimen banking programs in the U.S. and Germany are by far the most developed. In Japan, a small pilot bank is underway and in Canada a bank of frozen wildlife specimens exists which were collected during monitoring programs. At these meetings plans for future interactions between the existing pilot programs in U.S. and Germany were discussed. As a result of these meetings, we have initiated an interlaboratory comparison for the determination of chlorinated pesticide residues in human liver between NBS and three laboratories involved in the German specimen bank program. Samples from the two pilot banks have been exchanged for this purpose. In addition, aliquots of liver specimens from the NBS specimen bank are being analyzed in Germany for selected trace elements as part of an intercomparison. These sample exchanges will provide valuable information on the comparability of analytical data generated in the two banking programs.

As a result of NBS specimen banking activities, NBS researchers have been invited to participate in several additional workshops in related areas. As a follow-up meeting to the 1980 "Workshop on Research Needed to Improve Data on Mineral Content of Human Tissues" sponsored by the American Institute of Nutrition and the National Science Foundation, a workshop was held on "Protocols--Mineral/Element Analysis of Human Tissues" in 1981. The goal of this workshop was to prepare specific guidelines and protocols for sample selection, collection, preservation, and analysis of human tissues. The liver sampling protocol and homogenization procedures developed in the NBS pilot program were adopted at this workshop as models for the collection/processing of human tissue. NBS representatives also were invited to participate in an American Medical Association resource conference on "Trace Minerals: Current and Developing Concerns" and in an Advisory Group Meeting of the International Atomic Energy Commission on "Nuclear Techniques in Environmental Health Studies of Mineral Pollutants."

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S. A. Wise, Project Manager; K. A. Fitzpatrick, S. H. Harrison, W. F. Kline, S. F. Stone, R. Zeisler

The following members of CAC have participated in providing analytical research and data for the program during the past year:

C. F. Allen, S. N. Chesler, R. R. Greenberg, L. R. Hilpert, J. K. Langland, W. A. MacCrehan, E. A. I. Michaels, T. C. Rains, T. A. Rush

D. Service Analysis (11310 and 14304)

R. W. Burke

An important and unique activity within the Center for Analytical Chemistry is its service analysis function. Within the scope of this activity, the technical staff of CAC frequently gives advice, performs expert compositional analyses, and provides state-of-the-art calibrations on a very broad range of research and industrial materials. This service is openly available to NBS staff and to all federal, state, and local government agencies. In special instances where CAC has clearly demonstrated a unique analytical capability, this service is also available to private industry.

All requests for analytical services are handled initially by the service analysis coordinator who is responsible for discussing the measurement needs of the customer, recommending the most suitable approach, and indicating what the approximate costs will be. In instances where the analytical problem is quite complex or the analysis requires specialized considerations, the customer is placed in direct contact with the appropriate staff member for an in-depth discussion of the matter.

This is the twenty-first year that the service analysis program has existed as a formal program within the analytical chemistry group. Throughout this period, the technical staff has been, and continues to be, highly cooperative and dedicated to providing timely, informative, and cost effective analyses. A special effort continues to be made throughout the Center to provide this service with a minimum of disruption to on-going programs. Currently, the turnaround time for the more routine analyses ranges from a few days to about two weeks.

All analytical work is performed on a cost reimbursable basis. Within NBS, funds are transferred by an interdivision work order; outside work is handled by a purchase order. All billings are performed by the service analysis coordinator.

In FY 82, 114 service analyses were carried out by CAC staff at a cost of $226 K. In FY 81, the corresponding numbers were 134 analyses and a cost of $181 K. The most notable change in the number of requests was from within NBS where only 29 jobs were performed this year as compared to 51 in FY 81. This number of in-house requests reflects approximately a 50 percent decrease from the average number received in each of the three years immediately preceeding.

The service analysis function is broadly regarded by the CAC staff as an exceedingly important and integral part of its yearly activities. Not only does it fulfill a specific need for the customer, but also it provides an excellent means for NBS analysts to identify new and sometimes unfamiliar areas of emerging research and development that will require better analytical measurements and standardization for the future. The verification and recalibration of the gaseous and the glass transmittance SRM's that are performed under the service analysis function provides NBS with a long-term evaluation of their field stability and guarantees industry a continuing supply of these standards whose usefulness is extended considerably beyond the time period specified in the original certification. Additionally, several good research papers are published each year as spin-offs from the service analysis activities. At least two such papers are currently in preparation. One entails the preparation of accurate isotopic argon mixtures for interplanetary atmospheric measurements; the other involves the use of microanalytical techniques for examining the microcrystalline structure of cements and thereby elucidating their hardening mechanisms.

The argon work required the careful gravimetric-sequential flush preparation of two concentrations of gas standards having equal molar concentrations of argon-36 and argon-40. One mixture was prepared to contain 25 ppm of each isotope; the other contained 50 ppm of each. Both mixtures were stored in carbon dioxide at a pressure of 500 psi. Initially these standards will be used for the interlaboratory calibration of the mass spectrometers and the gas chromatographs involved in the analysis of the atmospheric samples that were brought back from the United States and the Russian missions to Venus in 1978. In the cement studies, members of CAC, using microanalysis and compositional mapping techniques, have studied the processes of mineralization in the hardening of cement pastes in conjunction with scientists from the Center for Building Technology. The formation of various minerals as a function of aging has been studied in order to ascertain the relationships between initial particulate size distributions and final solid state reaction products. A combination of quantitative microanalyses at arrays of points, combined with x-ray area scans, has been used for diagnostic analyses. Preliminary evaluation of the data indicates that the spatial distributions of the calcium hydroxide and the calcium silicate hydrate resemble that of the initial size distribution of the particulate tricalcium silicate used to make the pastes. This observation suggests that this initial distribution controls the solid state reactions over very long periods of time.

E. Laser Analytical Chemistry Group

1. Group Overview

The main objective of this group is to develop new approaches to performing accurate chemical analyses. Our primary emphasis remains on the use of lasers as highly selective and sensitive spectroscopic probes. In addition to our ongoing studies of the laser enhanced ionization in flames technique, we are collaborating with other Center staff on laser ionization mass spectrometric techniques.

The laser enhanced ionization (LEI) in flames technique has now been developed to incorporate computer wavelength control of two dye lasers, one of which was purchased this year. The two-photon excitation process shows detection limits at the 10 pg/mL level for most of the elements. Analyses of especially difficult to analyze samples have been performed with accurate results being obtained. We believe that the fundamental mechanism for signal collection is understood, and we are in the process of computer modeling the phenomenon with the objective of being able to predict the behavior of the mechanism which can then allow us to select parametric values of the LEI system to optimize its analytical capability.

A study of the tunable infrared diode laser has been completed. This project, which was started four years ago, was performed during a significant evolution of the diode technology. This technology has now been developed to a point where it can provide a useful system for chemical analysis. In previous years we had improved the stability of the laser and designed the optical system to minimize errors in the absorption spectroscopic technique. Recently, we have demonstrated the measurement of isotopic ratios and its utility in the highly selective Stark spectroscopy.

The group is collaborating with Center staff on a new project called material transport. The project was initiated as the result of studies made several years ago at NBS on the effluent of a spark discharge used for optical emission spectroscopy. When such effluent is passed into an inductively coupled plasma (ICP), a highly accurate analytical spectroscopic technique results. Apparently, the spark produces atomic vapor (e.g., from a metal sample) which condenses rapidly into very small particles which can be efficiently atomized in the ICP. This system, which has been developed commercially, has apparent high accuracy and reduces matrix effects as evidenced by the use of a single reference material for all iron bearing materials for example. We propose to characterize the matter produced by the spark with respect to type, amount and composition. If compositional bias between the components in the spark effluent and the sampled bulk material is minimal, experiments will be devised to determine the pertinent variables in the transport process. If the process can be understood, it may be possible to devise an atom reservoir that is amenable to accurate and sensitive quantitative spectroscopic analysis by several analytical methods including those utilizing a laser.

Emphasis will be placed upon the analysis of practical samples by the LEI technique while at the same time optimizing various parameters in the analysis system for quantitative analysis as contrasted to optimization for research purposes. Collaboration between our staff and that of the Divisions will continue in the areas of laser mass spectrometry, IR laser diode spectroscopy, and material transport phenomena.

J. R. DeVoe, Group Leader; G. J. Havrilla, R. McDiffett, F. C. Ruegg,
R. L. Sams, J. C. Travis, G. C. Turk, J. Wen.

2. Selected Technical Reports

a. Computer Simulation of Charge Transport and Current Detection Following Ionization in Flames (11310)

J. C. Travis

This project was undertaken in collaboration with Dr. Peter K. Schenck of the Center for Materials Science. A computer program was developed to simulate the transport of electrons and ions through a flame following pulsed ion formation by laser enhanced ionization (LEI). Sequential plots of the electron and ion distributions as a function of time provide a "movie" showing the response of both species to electric field, diffusion, and coulombic self-repulsion. In addition, the program computes the charge induced on each electrode by each of the charge distributions in the flame. The time derivative of this induced charge over the duration of the electron/ion dissipation process yields the predicted LEI signal pulse shape. Agreement of these pulse shapes with experiment over a variety of applied voltages, laser beam positions, etc., provides the primary evidence of the validity of the model, since no effective experimental probe of the actual LEI ion/electron distributions has been devised.

Figure 5 shows a typical frame of the ion/electron distribution "movie", 160 ns after the beginning of a 5 ns laser pulse occurring 0.3 cm from the cathode, with the anode located at 1.2 cm. The assumed initial electric field distribution corresponds roughly to 850 volts applied across a low background ionization flame (e.g. H_2/air). At 160 ns, the electrons may be seen to have moved about half of the distance from the point of origin to the anode, expanding considerably under the influence of diffusion. The ions have hardly moved nor diffused, reflecting the mass dependence of both mobility and diffusion. The effect of the ion and electron charge clouds on the internal electric field (through Poisson's equation) may be seen in the plot of the perturbed field. This effect was exaggerated by assuming the initial generation of a large number of ions and electrons by the laser, corresponding to the upper end of the dynamic range of LEI.

The electron and ion current signal pulses for the same simulation are shown in Figure 6. The electron pulse may be seen to drop to half current in about 350 ns, while the ion pulse (multiplied x 100 for display) peaks around 5 μs, and continues well beyond the 5.5 μs shown. The relative shapes and peak positions of the two pulses are complex functions of geometry and applied voltage, and agree qualitatively with experimental data.

The model has been particularly helpful in understanding the detailed nature of the interference to signal collection that is encountered when easily ionized matrices are aspirated. Specifically, such matrices modify the

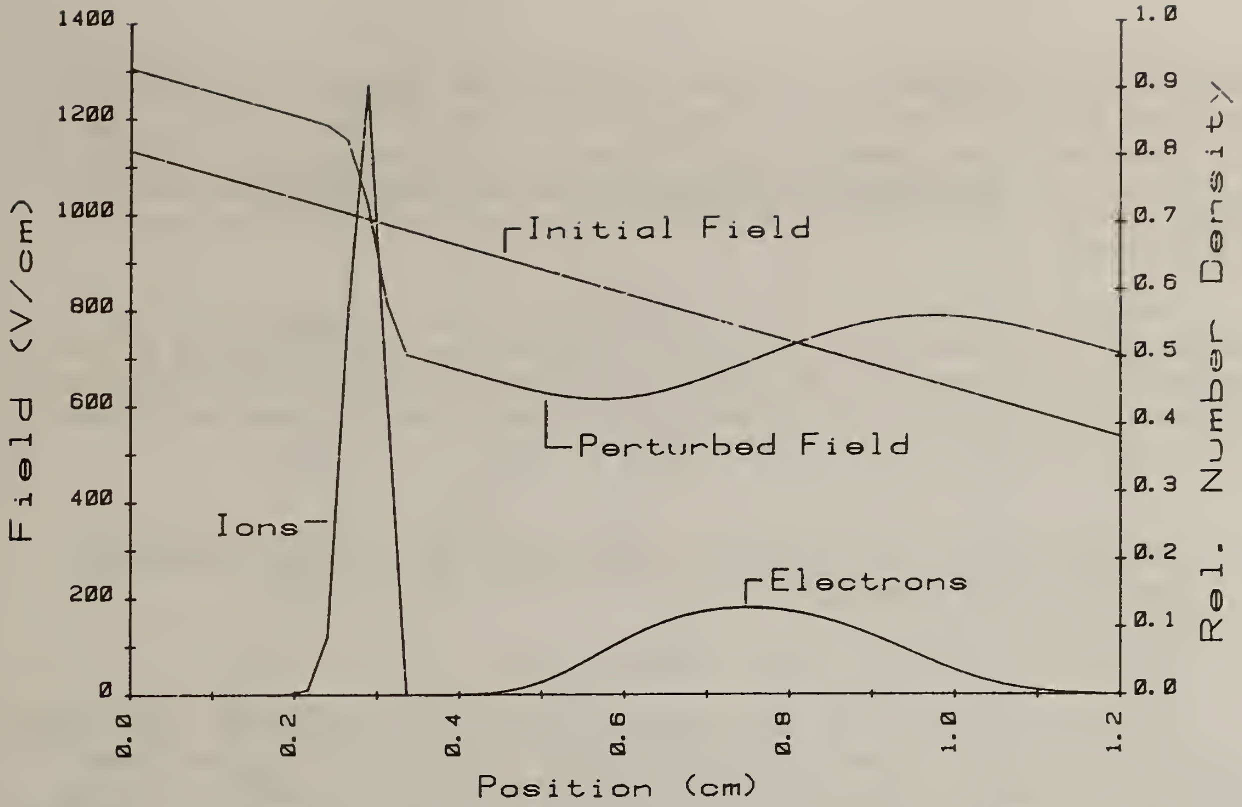

Figure 5. Plot of field (left axis) and relative number density (right axis) vs. distance from cathode for ions and electrons produced initially by laser beam at 0.3 cm. This plot represents a calculation of the state of the system at 160 ns after the leading edge of the 5 ns laser pulse.

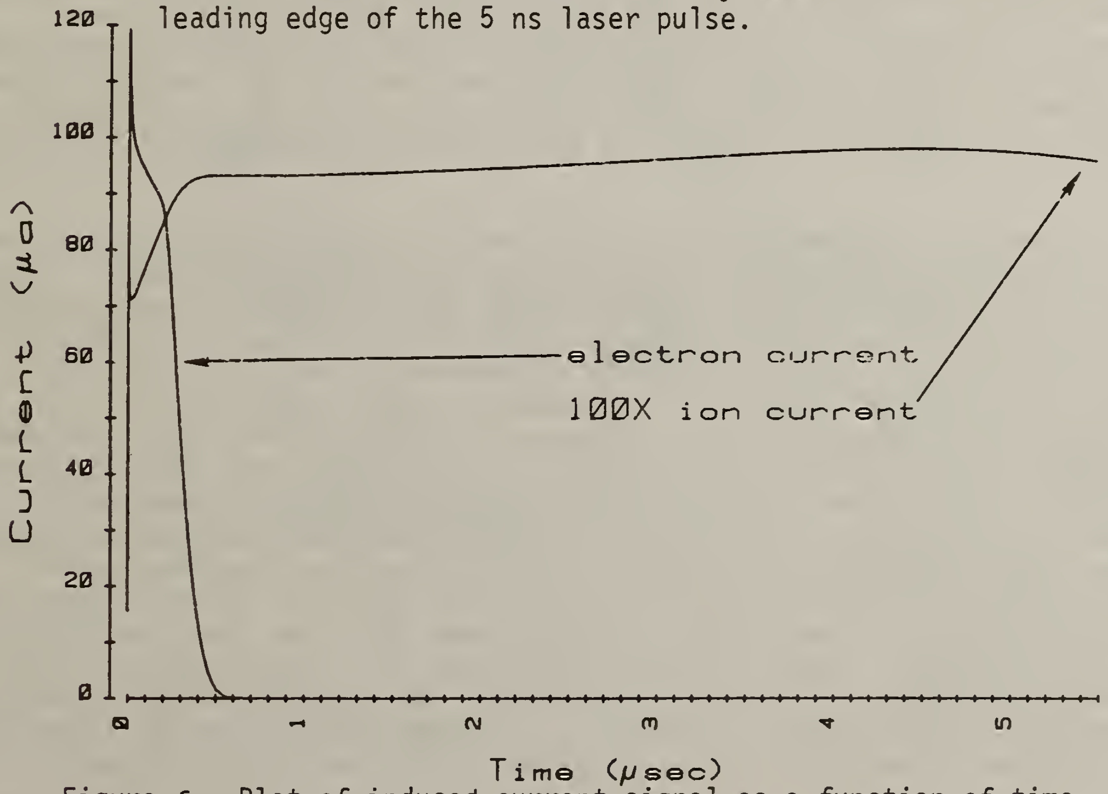

Figure 6. Plot of induced current signal as a function of time. The ion current has been multiplied 100X.

electric field gradient in the flame and change the current pulse profile. The model permits a theoretical study of the effect of beam position, applied field, and detection bandwidth on LEI signal. Such a study should permit optimization of experimental parameters to minimize such interferences, and should lead to the formalization of correction protocols for this type of matrix effect.

The model is presently being extended to include calculation of the background field from first principles. Further possible extensions of the program include increasing the laser pulse length to study the transient-to-steady state transition and inclusion of a second spatial dimension to more realistically model cylindrical diffusion.

b. Characterization of Pulsed LEI Current Detection and Implications for Analytical Measurements (11310)

George Havrilla, John Travis, Gregory Turk

Considerable effort has been devoted during the past year to understanding the details of how a signal is electronically registered when pulsed-laser enhanced ionization (LEI) occurs in an electrically probed flame. This has involved the development of a model which allows computer simulation of pulsed LEI signals along with experimental verification of this model under conditions likely to be encountered during analytical application of LEI spectrometry. Prior research on pulsed LEI has been done using signal processing optimized for sensitivity. The filtering and amplification procedures that were utilized, substantially distorted the shape of the LEI pulse, and much information regarding the signal detection process was lost. High time-resolution measurements of the LEI signal pulse have now been made with a minimum of electronic distortion, and comparison with theoretical predictions can now be made.

Following a laser pulse, two LEI current pulses are detected, the first is caused by the motion of the electrons and the second by the ions. Figure 7 shows an LEI electron pulse for 100 μg/mL of iron. The pulse duration, 300 ns, is considerably longer than the 10 ns laser pulse. It shows a sharp leading edge, limited by the response function of the amplifiers, with a trailing decay as predicted by the model. The observed double peak, which is not predicted by the model, appears to be caused by the electric field distribution between the electrodes in the flame. In the model, the field is assumed to follow a linearly decreasing function from the cathode to some point between the electrodes. In practice, the field has been measured and found to follow a non-linear and discontinuous function resulting from non-uniform flame composition. The corresponding ion pulse, shown in figure 8, peaks ∿6 μs after the electron pulse, with a peak amplitude ∿100 times less than that of the electron pulse. Again, the shape of the pulse is consistent with the modeled predictions. In terms of sensitivity, the ion peak is of no interest for analytical measurements, because it is a long pulse of low amplitude, and normally gated integration is used to observe only the electron signal.

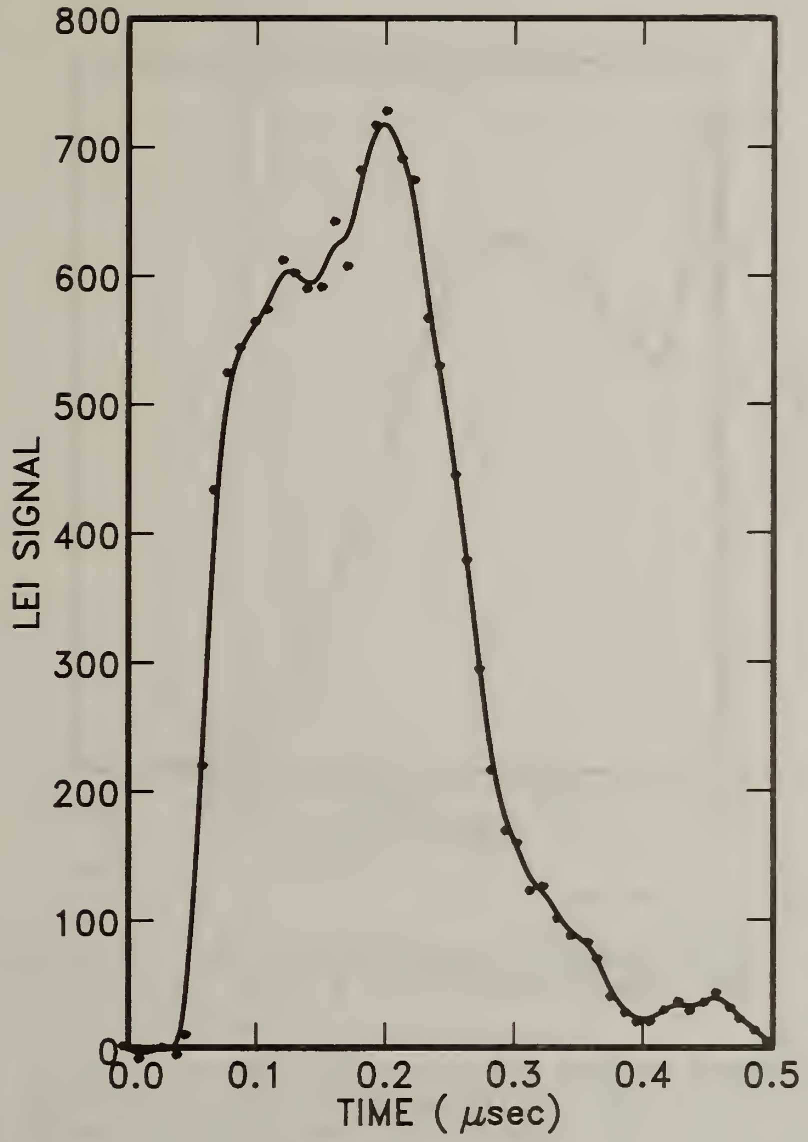

Figure 7. Laser-enhanced ionization electron pulse from 100 μg/mL iron.

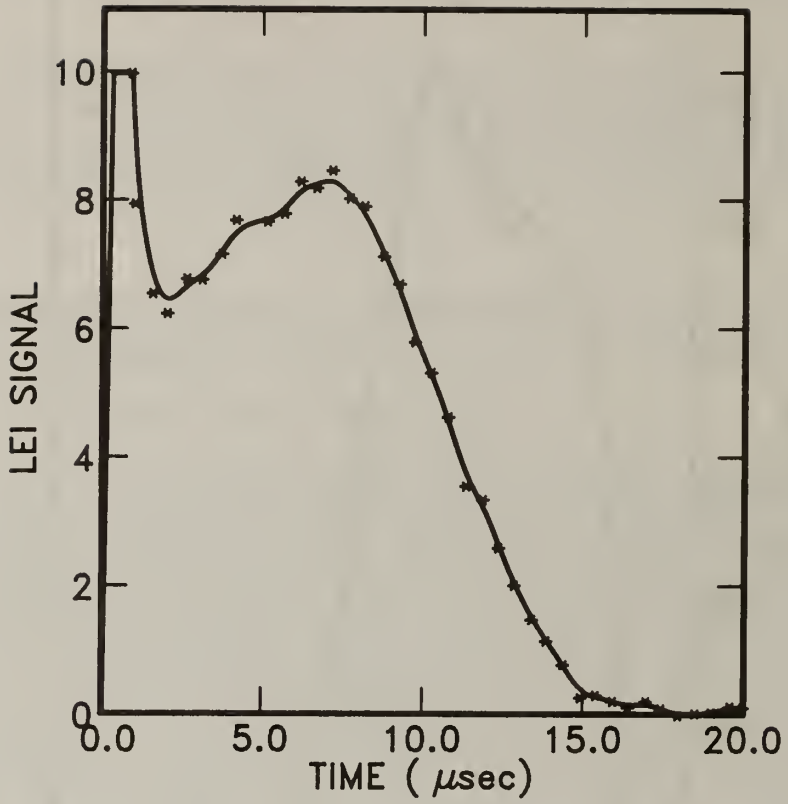

Figure 8. Laser-enhanced ioization ion pulse from 100 μg/mL iron. The truncated pulse at 0.2 μs is the electron pulse.

The shape of both the ion and the electron pulse is controlled by the magnitude and profile of the electric field in the flame, which causes the movement of the LEI charges. There are a number of experimental variables which affect the electric field magnitude and profile. Among them are the applied voltage, the electrode separation, the laser beam position, and the concentration of charged species present in the flame background. The latter of these variables is perhaps the most important because it can vary from sample to sample depending on the concentration of species in the sample which can be ionized by the flame without laser excitation, i.e. alkali metals. When alkali metals are aspirated into a LEI flame, the electric field tends to increase in the vicinity of the cathode, and decrease near the anode. Figure 9 shows LEI pulses observed for 100 μg/mL Fe with varying amounts of Na in the solution matrix when the laser beam is located near the cathode. With the beam in this position, the effect of increased Na concentration is to increase the electric field strength sensed by the LEI produced charged species.

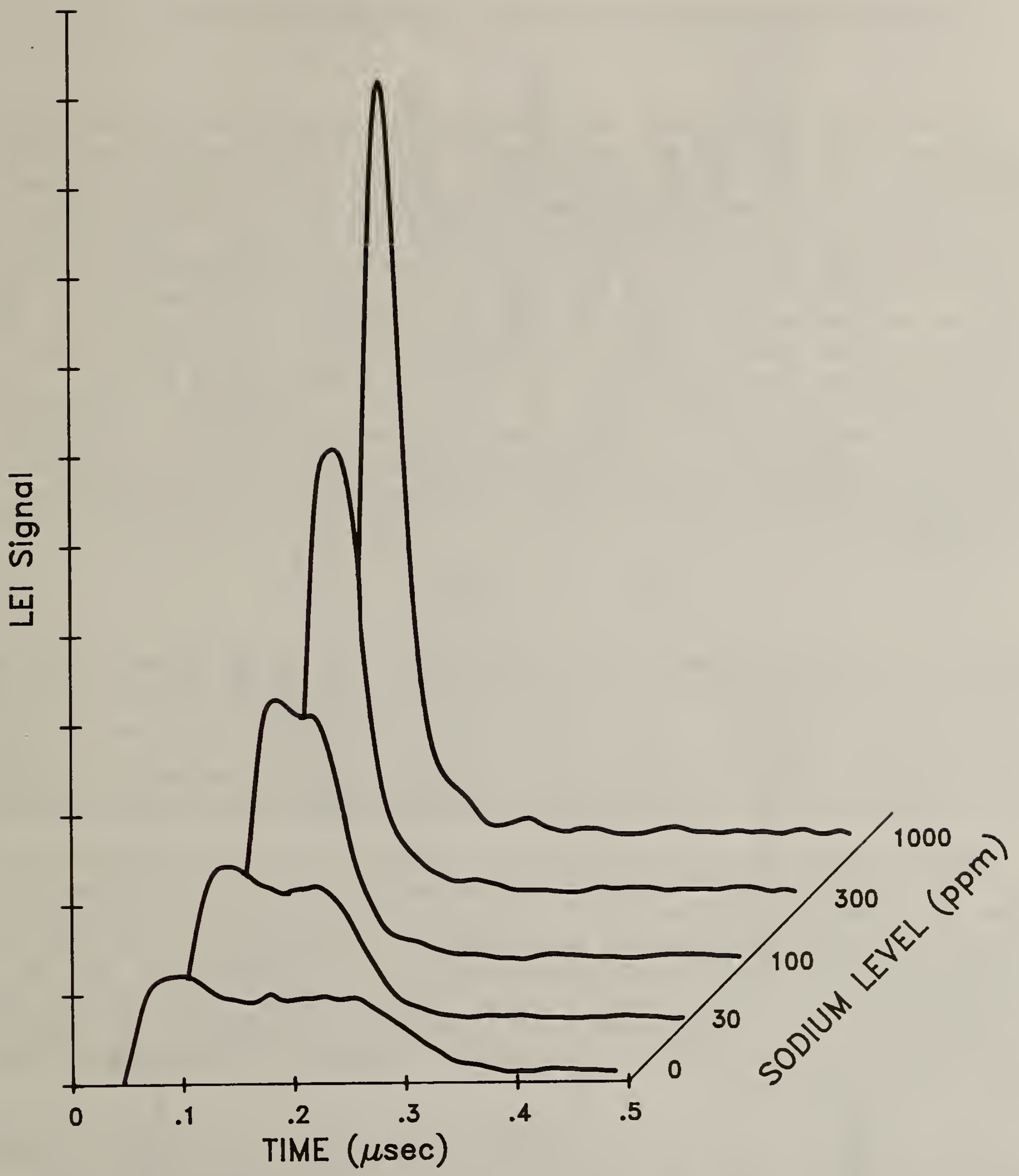

Figure 9. Laser-enhanced ionization electron pulses for 100 μg/mL of iron with varying levels of sodium present in the solution matrix.

This in turn moves the electrons toward the anode at higher velocities, inducing a larger signal current, but for a shorter period of time. The result is shorter pulse widths, with higher peak currents. The integrated pulse areas remain constant, except for the highest Na levels, where the electric field is so intense that the movement of the ions can be detected. Obviously for analytical application, a measurement of peak area will be less susceptible to matrix ionization interference than a peak height measurement.

c. Stark Modulated Infrared Diode Laser Spectroscopy (11310)

R. Sams

Diode laser spectroscopy (DLS) is nearly unsurpassed for the analytical detection and analysis of all trace gases, except homonuclear diatomics and noble gases. We have been able to measure analytes with relative abundances of 10^{-11} to 10^{-12} using a modest length multipass cell (28 transits with a basic path length) and second derivative detection technique. The selectivity of the technique, which is limited by the linewidth of the molecular transition, is a complex function of the number of molecules in the mixture to be analyzed and the relative positions and intensities of the transitions. The linewidth of the laser, which is very narrow relative to the width of the molecular energy level, helps only by improving deconvolution efficacy. If no analyte line can be found which is free of line interference from another molecule, it may be possible to isolate the molecular transition via Stark modulation spectroscopy. In this technique, an electric field is applied to the analyte molecule to cause a shift in the energy state of the molecule. For example, the first order, rotational energy level shift ΔW for symmetric top rotors is:

$$\Delta W = -\mu E \frac{MK}{J(J+1)}$$

where μ is the dipole moment, E is the applied electric field and J, K, M are rotational quantum numbers. For linear molecules the Stark effect is second order and is $\Delta W \propto \frac{\mu^2 E^2}{2Bh}$. Since values of B rotational constant and/or μ can vary by several decades, selectivity of analysis can be enhanced even if the Stark unshifted lines of analyte and interfering molecules overlap completely.

We are reporting on preliminary measurements using this technique, to show its ability to improve selectivity in analysis. The basic system is shown in figure 10 where the cell is replaced by a Stark cell consisting of two optically polished stainless steel plates 2.5 cm x 5 cm x 40 cm long in a vacuum housing. The plates are separated by six, 2-mm spacers. A high voltage gradient (1,000 - 50,000 volts per cm) is applied using one kHz sine wave modulation. A voltage modulation is applied to the plates and the diode is tuned through the transition of interest, thereby producing a conventional first derivative signal.

As a demonstration of this technique, ClCN, a molecule which has a large dipole (2.8 Debye), was used with an interfering molecule N_2O which has a small dipole (0.17 Debye). In figure 11, the spectra of these molecules are shown, each separately, both together, and with Stark modulation. It is seen that the Stark modulation spectrum is greatly simplified (only one major transition of ClCN remains). The selectivity has been greatly enhanced, but, the sensitivity is reduced. All linear molecules have small second order Stark effects. In other molecules, such as those with "symmetric top or rotors", the Stark effect is much larger. The sensitivity of this method with these molecules should be comparable to DLS with a significant improvement in selectivity and thereby inherent accuracy.

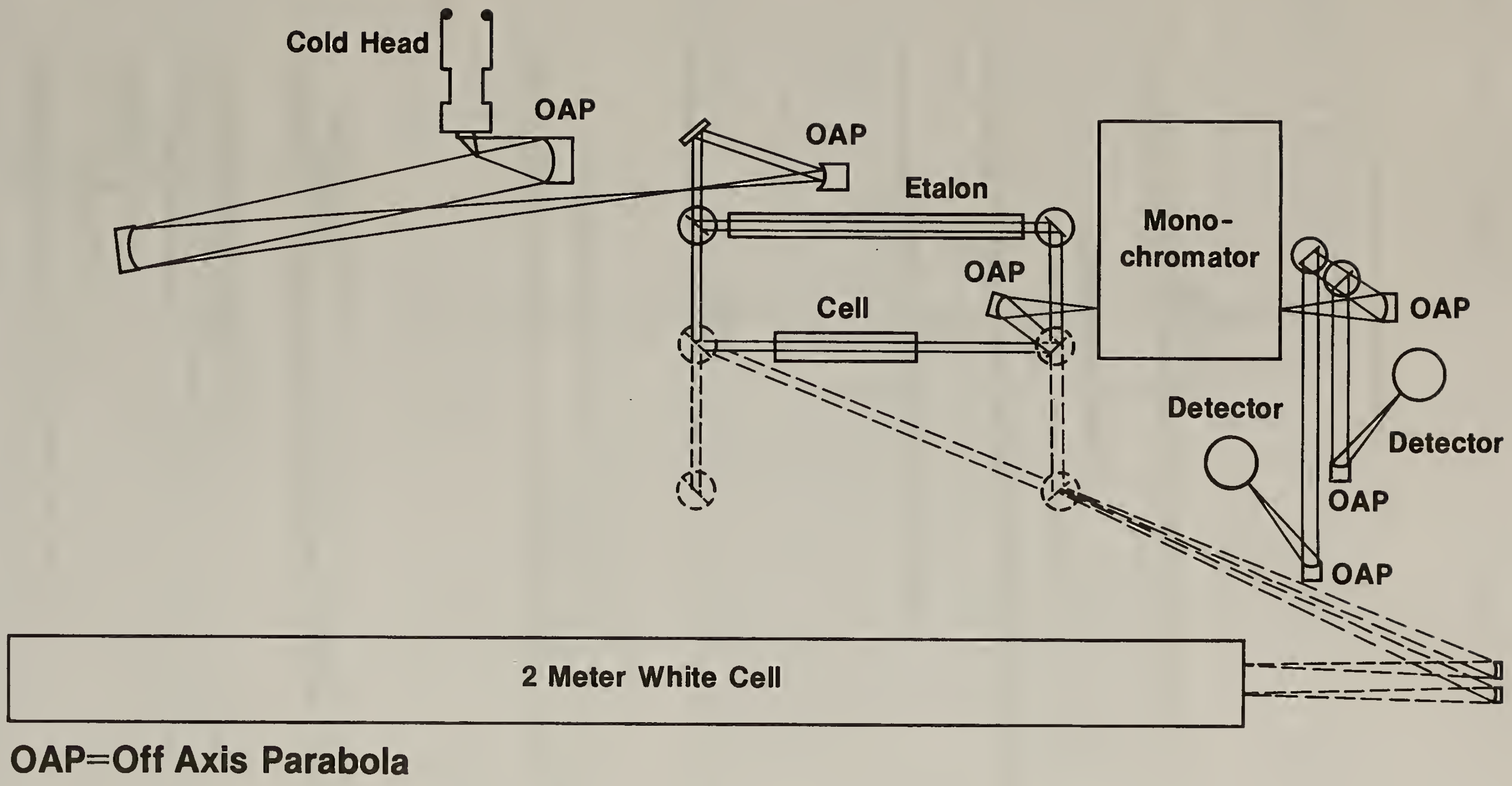

Figure 10. Diode laser optical system.

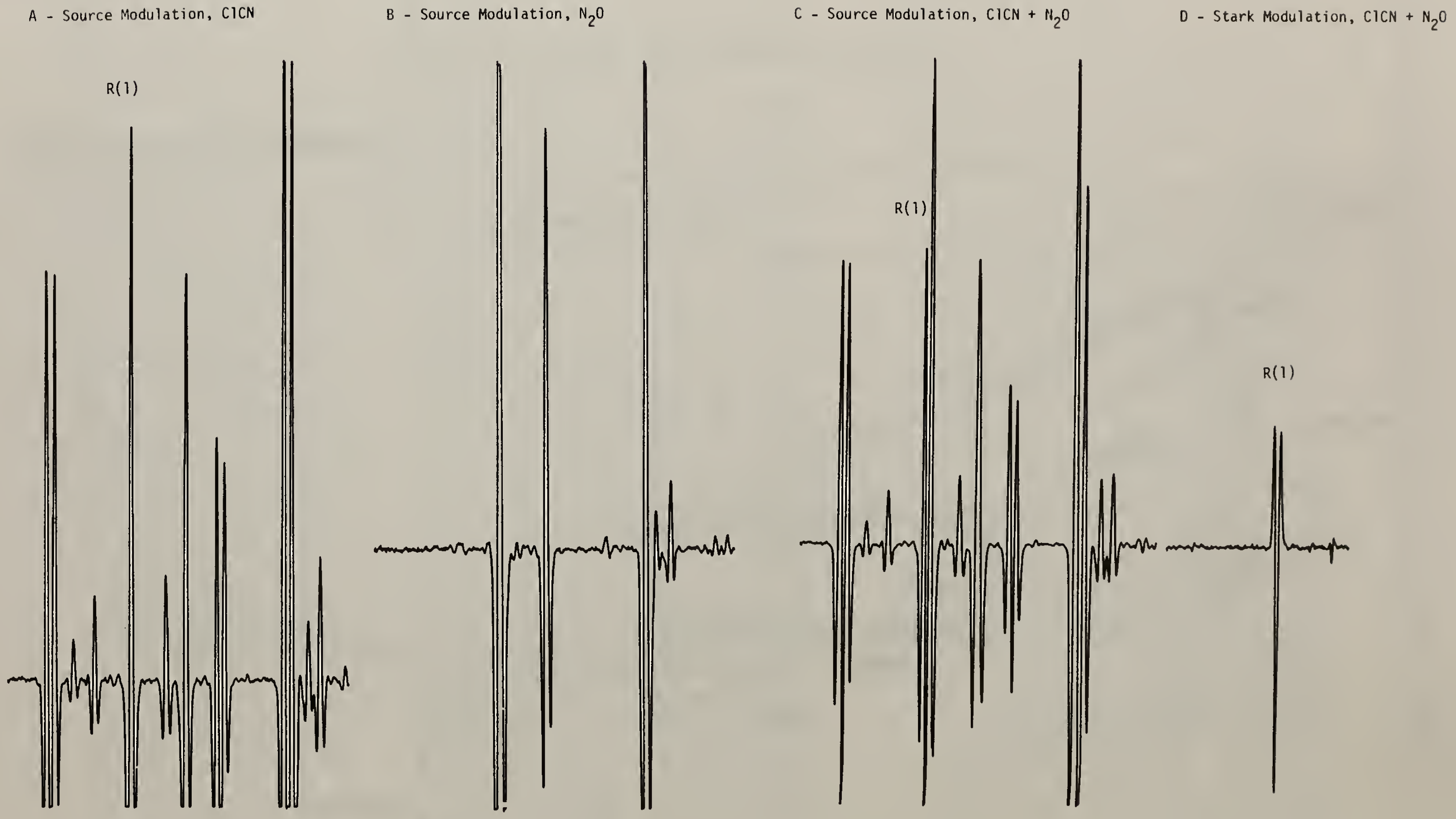

Figure 11. Infrared strip chart absorption plots of intensity (arbitrary units) vs. wavelength. A, B, and C show spectra without Stark modulation. Almost perfect line overlap is observed at the position of the Stark modulated line D. The Stark modulated line which is free from interference is located at 2216.4 cm^{-1} and is the R(1) ^{35}Cl line.

d. Measurement of the Isotopic Ratios: $^{12}C/^{13}C$ and $^{14}N/^{15}N$ (11310)

R. Sams

Using the laser diode system described in last year's annual report, we have demonstrated the reproducibility of the isotopic ratio measurements of $^{12}C/^{13}C$ in CO_2 and $^{14}N/^{15}N$ in N_2O to about 0.1 percent. Several methodologies which utilize our recently completed microcomputer system were evaluated and we report here on two which produced the best results.

The first method (signal averaging) was to scan the diode wavelength at a rate of one point per 160 microseconds and average the data normally over 1000 scans of 256 points each. In using this technique we were forced to D.C. couple the InSb detector to the data collection system because A.C. coupling severely distorted the signal, prohibiting accurate measurements. The detector has a D.C. offset, caused by normal background radiation, which has to be back biased to maintain a significant dynamic range. There was also a small drift in the D.C. level which produced a small error in the data. The relative ratios of $^{12}C/^{13}C$ and $^{14}N/^{15}N$ using this technique are given in Table 4 along with the standard deviation of the measurements. Since different diodes were used for the two gases, and each diode has its own wavelength instability, slightly different errors result. The reported errors are the standard deviations of the average of a group of 10 measurements consisting of 1000 sweeps each. The reported ratios are those of the maximum intensities of each line. Absolute ratios of ^{12}C to ^{13}C or ^{14}N to ^{15}N can be derived from line intensity measurements, but the signal averaging method is best suited to measure the ratio relative to a known standard.

Table 4. Isotopic Ratio Measurements.

Molecule	Transition	Band	Lock and Jump Ratio	Signal Averaging Ratio
$^{12}C^{16}O_2$	P (34)	$10^{0}1-10^{0}0$	----[a]	2.70370 (0.0830)[c]
$^{13}C^{16}O_2$	R (36)	$01^{1}1-01^{1}0$		
$^{14}N_2{}^{16}O$	P (10)	$02^{0}-02^{0}0$	1.1528 (0.00009)[b]	1.1522 (0.00024)[c]
$^{14}N^{15}N^{16}O$	R (11)	$00^{0}1-00^{0}0$		

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[a] Lock and jump method not developed at time of these measurements.

[b] Error in parentheses is one standard deviation of the average based on 49 degrees of freedom.

[c] Error in parentheses is one standard deviation based on 9 degrees of freedom.

The second method (lock and jump) was to lock the diode frequency to the transition of interest by using a cell containing the analyte and by using conventional locking to the first derivative of the absorption signal. The same transition was then measured in a sample cell using the second derivative of the absorption signal. The diode was modulated at 9.1 kHz and twice this frequency was used in the lock-in amplifier to achieve the proper signal. Forty measurements of an absorption peak were computer averaged. The diode was then unlocked and jump tuned to the other appropriate transition and relocked. Again, forty measurements were taken and averaged. The ratio was then computed and the process was repeated fifty times. The average value and its reproducibility are shown in Table 4. The lock-jump technique was not developed at the time of the carbon isotopic ratios. However, it worked very well for nitrogen.

The amount of sample required is quite small; approximately 200 nmoles for N_2O and 400 nmoles for CO_2. The samples can be recovered if necessary. Ratios of other atoms, ${}^{16}O:{}^{17}O:{}^{18}O$, are easily measured in both CO_2 and N_2O.

It has been demonstrated that relative isotopic ratios of ${}^{12}C/{}^{13}C$ and ${}^{14}N/{}^{15}N$ can be measured to a precision of approximately 0.1 percent relative standard deviation of the average using a laser diode system. A major factor which limits the accuracy is the temperature control of the diode system. Long term (more than one hour) temperature stability (better than 0.2 K) is required if an accuracy of better than 0.05 percent is to be attained.

3. Outputs and Interactions

a. Publications

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Maki, A. G. and Sams, R. L., "High Resolution Infrared Spectrum and Structure Determination for Carbon Diselenide (CSe_2)", J. Mol. Spec. 90, 215-221 (1981).

Frommer, C., Lovejoy, R. W., Sams, R. L., and Olson, W. B., "The Infrared Spectrum of the ν_1 Band of SiD_3H", J. Mol. Spec. 89, 261-267 (1981).

b. Talks

Travis, J. C., "Laser-Based Methods for Ultra-Sensitive Detection of Atomic and Molecular Absorption", 11th ACS Northeast Regional Meeting, Rochester, N.Y., October 21, 1981.

Travis, J. C., Turk, G. C., and DeVoe, J. R., "Toward Real Sample Analysis by Laser Enhanced Ionization in Flames", Eastern Analytical Symposium, New York, N.Y., November 18, 1981.

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Elkins, J. W. and Sams, R. L., "Measurement of Nitrous Oxide and Halocarbons F-11 and F-12 by Fourier Transform Infrared and Tunable Diode Laser Spectrometers", IX Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 23, 1982.

Travis, J. C., "Optogalvanic Spectroscopy", NATO Advanced Study Institute on Analytical Laser Spectroscopy, Erice, Sicily, Italy, September 23, 1982.

c. Committee Assignments

James R. DeVoe
NBS Committee on Selection of Microprocessors for the Storeroom

Fillmer C. Ruegg, Jr.
NBS Committee on Selection of Microprocessors for the Storeroom

Gregory C. Turk
CAC Colloquium Committee

II. Inorganic Analytical Research Division

Ernest L. Garner, Chief
Barry I. Diamondstone, Deputy Chief

A. Division Overview

The diverse analytical methodology in the Inorganic Analytical Research Division is organized functionally into four broad areas; activation analysis, atomic and molecular spectrometry, analytical mass spectrometry, and electroanalytical chemistry. This structure provides both the flexibility and the analytical capability to address a wide variety of research problems, as well as to carry out the full range of analyses required by NBS, and for other Federal agencies and other institutions, either private or public, when requested and appropriate. Working within this framework to provide maximum public benefit, the research and measurement priorities of the Division are established on the basis of: (1) advancing and maintaining analytical chemical metrology, (2) providing the basis for chemical standardization, and (3) addressing the need for accurate chemical characterization of inorganic species to make a substantial contribution to solving problems of national importance confronting government and industry.

Substantial progress has been made within the Division in the area of competence research. Considerable effort has been put forth to establish neutron depth profiling as a tool for compositional mapping and to investigate ion structures/mechanisms as a means of developing a better understanding of the basic processes in thermal ionization mass spectrometry. In addition to these competence activities, now in their second year, a first year effort has been initiated to investigate sample transport processes in spark discharges. Potential benefits to be derived from this research include a decrease or elimination of matrix effects and identification of spark source variables that produce systematic errors. The total competence effort has already paid significant dividends in terms of new findings in the laboratory, establishing collaborative research with other institutions, attracting visiting scientists and postdoctoral candidates, and developing related programs sponsored by other government agencies. As one of several examples, visiting scientists and postdoctoral candidates have made significant contributions to the establishment of the depth profiling facility and to the measurement of selective elements using resonance ionization mass spectrometry.

With competence research as the cutting edge for exploring new directions in analytical chemistry, other research efforts are directed toward targets of opportunity to maintain and improve chemical metrology. This diversified program covers atomic weight research, inorganic constituents in steel processing wastes, recycled oil, trace metals in waste materials, NDE dye penetrants, specimen bank research, and methods research for certifying a variety of SRM's. For example, major achievements in the area of methods research include development and successful application of isotope dilution mass spectrometry (ID/MS) for trace quantities of iodine in biological materials, analysis of ultratrace concentrations of cadmium in blood, and the improvement of analytical procedures for ultratrace levels of chromium. New facilities include a laboratory for high accuracy pH measurements and a modern facility for the determination of gases in metals. The addition of these two facilities will help to reestablish widely needed capabilities that have not been available at NBS for the last decade. Continued evaluation and application of the Compton suppression technique has improved detection limits and provided increased sensitivity for selected elements such as chromium, aluminum, zinc, and vanadium. Each of these achievements have substantially enhanced the quality of trace element determinations performed on a regular basis in the Division.

As in past years, the Division has provided major analytical services for the certification of SRM's. The magnitude of this involvement is reflected by analyses carried out on more than 75 different SRM's covering many of the material types and most of the major categories of the inventory. In addition to measurement services for SRM's, significant contributions were made to the preparation and characterization of materials for use as quality assurance standards for other government agencies. Of particular significance has been the development, preparation, and distribution of the first synthetic sludge material for use as a quality assurance standard in the characterization of priority elements in waste residues. This particular standard is but the first in a series leading to the ultimate certification of a much needed material that exhibits the characteristics and matrix effects found in a "real world" waste material. Other measurement services have been provided to complete or support commitments to broad-based programs in environmental measurements, resource recovery, and recycled oil. During the coming year measurement services for these latter areas will be reduced and/or replaced by other commitments.

New opportunities for other agency research and services are being developed or explored in promising areas such as glass standards for nuclear waste storage, resonance ionization mass spectrometry, iodine at ultra-trace levels, and methods development to determine toxic/essential nutrient elements in food/health materials. One of the more promising and far reaching new areas is tracer studies for acid precipitation. This effort will seek to develop a means of identifying the sources and tracking the fall-out of sulfur using unique isotopic and elemental ratioing schemes. In addition, increased emphasis will be placed on the development of stable reference materials and analytical protocols to characterize pH, conductance, acidity, and trace metals in acid precipitation.

For the immediate future, a nearly equal split between research, the certification of Standard Reference Materials, and analytical support for problems of national importance will constitute the major portion of the Division's programs. As in previous years, new proposals will be directed at other government agencies in a manner which will complement on-going and long-term research. In addition, the Division will pursue, in collaboration with the Center, those areas of analytical chemistry which have been identified in the long-range planning process as appropriate for increased growth or new directions.

1. Activation Analysis Group: Overview

The principle objectives of the Activation Analysis Group continue to be the development of nuclear analytical techniques for better sensitivity, higher selectivity, and increased accuracy. A high level of competence has been developed for various reactor-based activation analysis techniques which include instrumental and radiochemical neutron activation analysis (INAA and RNAA), prompt gamma activation analysis (PGAA), and the nuclear track technique (NTT). Non-reactor-based techniques include photon activation analysis (PAA), fast neutron activation analysis, and charged particle activation analysis, which have been used on a more limited scale. With this wide variety of techniques, support is provided for the diversified NBS and other agency programs requiring analytical measurement services. For example, simultaneous multielement determinations over a broad dynamic range in complex matrices as well as highly selective determinations of constituents in the sub-nanogram range have been provided for programs such as Standard Reference Materials, Environmental Measurements, Recycled Oil, Resource Recovery, Nuclear Safeguards, and other disciplinary research programs at NBS.

During the past year, major research efforts have been directed toward the demonstration of multielement capabilities of INAA procedures. With an appropriate combination of PGAA and several INAA determinations, at suitable irradiation and decay intervals, it has been possible to determine more than thirty trace elements in such diverse matrices as liver homogenate, coal, fuel oil, and air particulates. Recent research on instrumental means for background reduction complemented these activities. The evaluation of the newly acquired Compton suppressor system for application to multielement determinations resulted in increased sensitivity for several crucial elements. The continuing evaluation of compton suppression techniques using specific detector combinations will provide unique activation analysis sensitivities for such elements as Al, V, Cr, Ni, Zn, and Pt.

Considerable effort has been spent in support of the Pilot National Environmental Specimen Bank (NESB) program. The cryogenic homogenization technique has been improved to accommodate samples up to 1000 g. Sieving experiments at cryogenic temperatures have supported the previous data which had indicated that homogenates processed in the newly developed Teflon disk mills will pass a 40 mesh sieve. The on-going evaluation of the trace element baseline data collected during the first year showed some interesting trends due to the variations in the sample population. For future analyses, a selection of samples which better match epidemiological population data will be considered. Activation analysis data are currently being evaluated to determine the effects of the first year of storage. The second year collection baseline analyses have been initiated using improved instrumental multielement techniques.

The development and installation of the neutron beam depth profiling facility and the first determinations of depth profiles in collaboration with other researchers in the competence program is another important step towards the continuous expansion of research activities. There is a significant potential in exploring this and other "unconventional" activation analysis techniques for future applications especially in the important areas of materials research. To match future needs in high purity materials, gases in metals and distribution of elements, more research must be conducted in the areas of "unconventional" use of reactor neutrons as well as in the use of non-reactor activation sources.

Research efforts during the coming year will focus on the extension of the multielement procedures. For example, the measurements needed to characterize the irradiation facilities after the planned increase of the NBS reactor power to 20 MW will be used to initiate and evaluate "absolute" or monitor activation analysis. This technique will provide results on more elements, since the occurrence of unexpected elements will not preclude their quantitation. For the NESB specimens, an optimized analytical protocol will be developed which can overcome the restrictions of this specific matrix. In the area of non-conventional activation analysis, the use of a fast transfer system for analysis via very short-lived isotopes will be evaluated. It is also anticipated that procedures for the determination of gases in metals will be investigated. However, in this area, access to a source of fast neutrons and/or charged particles is necessary.

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2. Analytical Mass Spectrometry Group: Overview

The primary objectives of the Analytical Mass Spectrometry Group are the development and maintenance of capabilities for high accuracy isotopic ratio measurements and the application of these measurements to analytical chemistry. The increasing need for high quality analytical measurements on sub-microgram amounts of material requires continual improvement in chemical separation and purification techniques and mass spectrometric instrumentation. To accomplish these objectives, the Mass Spectrometry Group is composed of essentially two sub-groups. The chemistry sub-group is responsible for all of the chemical aspects of the Groups work. Separation science, isotopic equilibration, sample dissolution, purification, and "contamination-free" sample handling are primary concerns in this area. The instrumental sub-group specializes in inorganic mass spectrometry. This sub-group has considerable expertise in high accuracy mass spectrometric isotope ratio measurements and is responsible for developing improved methodology and instrumentation for thermal ionization, spark source, electron impact and surface ionization mass spectrometry.

During the past year, the Group continued to have a favorable balance between research and analytical samples due primarily to the research funds for the investigation of ionization mechanisms and ion structures received through the Competence Building Program. During FY 82, work on the laser mass spectrometer neared completion. Pulsed and CW laser sources have been installed and two mass spectrometer systems, a time-of-flight (TOF-MS) and a magnetic sector, have been assembled. Research output from the laboratory, has included the multiphoton ionization of acetone and residual gases using the TOF-MS and the first reported formation and measurement of Mo^+, Re^+, and V^+ ions using resonance ionization mass spectrometry (RIMS).

Research in ion optics progressed considerably during this year. A more accurate formulation of the magnitude and extent of magnetic stray fields has been developed. This has been incorporated into a large computer program that solves the basic equations of motion of charged particles in a magnetic field. As a result, refined calculations of the geometrical parameters of existing instruments have been performed with resultant improvements in the design of new instruments. A program to display graphically the ion beam movement is currently under development.

Progress has been made on the modification of instrumentation and on the development of fully automated, high accuracy mass spectrometers. Improved filament controls have been installed on most of the thermal source mass spectrometers. Performance has been excellent with "down-time" reduced nearly to zero. An improved emission regulator has been designed and constructed and is currently under evaluation. Tests of a computer system for controlling the filament temperature have been successfully completed. The first digital, automatic gaussmeter/controller has been constructed and is currently being calibrated.

An automated gas source mass spectrometer with a triple collector is nearly ready for operation in the normal mode with full automation expected in the near future. A new, fully automated, manifold system and inlet system for this instrument has been completed and is under test. Computer interfaces for both systems are under construction.

In the area of isotope ratio measurements, work is progressing toward a redetermination of the atomic weight of gallium. High-precision methods have been developed for both the assay and mass spectrometry of gallium. Improved methodology for isotope dilution mass spectrometry (ID/MS) continues to be a major output of the Group. The first ID/MS method for trace iodine in botanical materials has been developed and applied to the determination of iodine in SRM 1572, Citrus Leaves. The newly developed thermal method for sulfur has been applied to biological and environmental SRM's. Ultra-trace concentrations of cadmium in blood have been determined by high-sensitivity (pulse-counting) mass spectrometry. ID/MS determinations of chromium have been extended to the ultra-trace level.

In several key areas, research and measurement activities were augmented by long term guest workers. For example, Dr. Pedro Morales of the Institute of Physics, University of Mexico has been working on magnetic stray fields and gas source mass spectrometry. Mr. Eddy Michiels of the Central Bureau for Nuclear Measurements, Geel, Belgium, worked on lead in foods and cadmium in blood. Ms. Emile Deal, a guest worker from the Smithsonian Institution, Washington, DC, is working on the determination of provenience of artifacts by lead isotopic ratios. In addition, several scientists have visited NBS for extended periods, primarily for enrichment in state-of-the-art isotope dilution mass spectrometry.

Again this year, expertise was utilized for several programs that support mass spectrometry. A new pure-reagents laboratory was completed and is supplying ultra-pure acids and solvents to fulfill the needs of analysts within the Division as well as those in outside laboratories. A study of the precision and accuracy of Kjeldahl nitrogen determination in steel SRM's is currently in progress. The efficiency of oil extraction from mill scale is under investigation. The project on trace element characterization of the Chesapeake Bay was completed with the evaluation of the particulate data which produced specific relationships between elements and groups of elements. A precise leach test for a proposed glass nuclear waste reference material was developed.

Research plans in the immediate future will focus on ion mechanisms, ion optics, atomic weights, and the development of chemical and mass spectrometric procedures for isotope dilution analysis. Competence plans include research on the processes controlling resonant ion formation using thermal atomization sources, interpreting anomalous resonant ion formation, and applying the RIMS capabilities to studies of atomic and molecular vaporization and ionization in thermal sources. Research is also planned to investigate negative ion mass spectrometry using complex emitting surfaces and to develop methodology for the utilization of negative ions in the presence of high electron current densities. Another significant project is the development of a fully automated, digitally controlled, off-axis mass spectrometer. The improvement of spark source measurements by simultaneous dual collection of ion currents and by high speed peak switching will be investigated. Completion of the redetermination of the atomic weight of gallium is planned and measurements leading to a redetermination of the atomic weight of lithium will be initiated. New chemical separation techniques and mass spectrometric methodology to lower detection limits and to increase the library of elements determinable by ID/MS will be given major attention.

Thomas J. Murphy, Group Leader; I. Lynus Barnes, Ellyn S. Beary, William A. Bowman, III, Karen A. Brletic, Emile C. Deal, John D. Fassett, John W. Gramlich, Emerson F. Heald, William R. Kelly, Howard M. Kingston, George M. Lambert, Lawrence A. Machlan, John R. Moody, Larry J. Moore, Pedro A. Morales, Paul J. Paulsen, Lura J. Powell, Ronald W. Shideler, Mary E. Stone

3. Atomic and Molecular Spectrometry Group: Overview

The Atomic and Molecular Spectrometry Group faced with an ever increasing demand for improved accuracy and sensitivity, continually strives to develop new techniques for spectrochemical analyses. Efforts towards achieving this goal have primarily been in the areas of sample preparation, matrix modification, and expanded multi-element capabilities.

A significant effort has been expended in the area of the inductively coupled plasma (ICP) and the direct current plasma (DCP)/echelle spectrometers to improve analytical measurements and basic methodology. A major accomplishment has been the development of a system which thermally regulates the DCP/echelle spectrometer. This system largely eliminates intensity drift due to shift in wavelength. In addition, the development of a matrix buffering technique has improved the accuracy of the analytical measurement. To isolate variability in the ICP, on-line analysis of variance (ANOVA) software has been developed.

Atomic absorption (AAS) with electrothermal ionization has a high sensitivity for approximately 45 elements. However, the technique is subject to many chemical and inter-elemental interferences. Matrix modification techniques have been developed to alleviate many of the interferences and to improve the accuracy of the analytical measurements. Research to develop a universal matrix modifier to eliminate interferences in graphite furnace AAS was initiated two years ago and is still in progress. Methods have been developed, in conjunction with an adaptation of the L'vov platform, to minimize most of the interferences encountered with electrothermal atomization for all priority pollutants encountered in environmental and biological materials. The combination of the L'vov platform and matrix modification has led to improved accuracy and sensitivity for trace elemental analysis.

In molecular spectrometry, significant progress has been made in the production of SRM quality metal-on-quartz transmittance standards. This year, a number of sets of this SRM (2031) will be available for issue. In a closely related effort, the calibration of SRM 930, glass filter transmittance standards, is continuing. More than 1000 sets of this SRM have been issued since its introduction in 1970; approximately 50 sets are returned yearly to this Group for verification or recalibration. Research is in progress to produce several types of fluorescent glass standards for use in nondestructive crack testing. The major development in this area has been the decision to switch from the previously studied uranyl-doped silicate glass to a terbium-doped phosphate glass as the basis for these standards. The fluorescence-temperature coefficient of the terbium glass is at least an order of magnitude less than the uranyl glass and should be usable with no auxiliary thermostating, even under conditions where temperature changes are as large as 20 °C.

Major areas of involvement of the Atomic and Molecular Spectrometry Group have been in the characterization of Standard Reference Materials, participation in programs of national concern, and the performance of service analysis. A few of the Group's accomplishments this past year have included the application of spark emission spectrometry to the acceptance testing, homogeneity testing and elemental analysis for the SRM metal program, and the utilization of AAS, ICP, and DCP for homogeneity testing, and characterization of minor and trace elements in metals, envionmental, and biological SRM's. AAS with electrothermal atomization and matrix modification was used to survey the concentrations of 11 elements in 56 different FDA injectable materials and to provide analytical data on specimen bank samples, acid rain standards, and hazardous waste leachate solutions. DCP was used to determine 12 elements in 30 leachate solutions from glasses proposed as formulations for nuclear waste encapsulation. Spark emission spectrometry and combustion techniques for carbon and sulfur analysis were used to determine the composition of the structural steel involved in the accident at the Hyatt Regency Hotel in Kansas City.

Future research will place greater emphasis on understanding and controlling the fundamental excitation process occurring in atom-production sources. Other activities will include the development of a solid sampling technique to be used in conjunction with ICP for the elemental analyses of biological tissues and fluids, the improvement of the precision and accuracy of DCP by the use of internal standards and improved nebulization systems, the evaluation of an ICP/AFS system for multi-element analysis, the evaluation of a gas generation procedure for DCP, the evaluation and method development of state-of-the-art instrumentation for carbon, sulfur, hydrogen, oxygen, and nitrogen in metals, the intercomparison of physical methods for verifying photometric linearity, the extension of the capability of the high-accuracy spectrophotometer to the near-infrared region, the investigation of group separation using non-selective chelating agents as a basis of shortening the chemical preparation for multielement isotope dilution mass spectrometry, and the development of a universal matrix modifier to AAS with electrothermal atomization. In addition, a major effort will be made to use the Zeeman/atomic absorption spectrometer for analyses of metals in high-solid matrices and to study metal ion speciation for As, Cr, and Zn in a variety of materials using a hybrid AAS unit.

Theodore C. Rains, Group Leader; Carol G. Blundell, David E. Brown, Robert W. Burke, Therese A. Butler, Barry I. Diamondstone, Michael S. Epstein, Radu Mavrodineanu, Jerry D. Messman, Kimberly I. Moran, John A Norris, Douglas J. Patin, Theresa A. Rush, Roger M. Stone, Robert L. Watters, Jr.

4. Electroanalytical Chemistry Group: Overview

The objectives of the Electroanalytical Chemistry Group are the development and application of electrochemical principles for chemical analysis. The techniques employed include amperometry, conductimetry, coulometry, ion chromatography, potentiometry, and voltammetry. Research activities are directed toward attaining a more thorough understanding of the complex chemical systems encountered during the development and implementation of high-accuracy analytical procedures ranging from ultra-trace determinations in a myriad of matrices to assays of ultra-pure chemicals. The popularity and utility of electrochemical techniques for chemical analysis is expanding due to advances in technology. The Electroanalytical Chemistry Group intends to take an active role in this expansion through innovative research that incorporates all of the techniques described above. Emphasis will be in the areas of speciation, multi-component analyses, and measurement assurance.

This year a major effort has been expended in re-establishing the capability for making high-accuracy pH measurements. The necessary instrumentation has been assembled, tested, and calibrated. Highly stable silver/silver chloride reference electrodes have been prepared for use in the emf measurement cells without liquid junctions. Preliminary measurements have been made on solutions of dilute mineral acids and of standard pH buffer materials in anticipation of an extensive recertification program that is scheduled for next year and which will involve several of the Standard Reference Materials (SRM's), pH and pD buffers, which are now in short supply. One of the materials, the sodium carbonate/sodium bicarbonate pair, has already undergone acceptance testing. This new pH facility will also enhance our ability to conduct pH research in conjunction with the Acid Rain Program.

High purity arsenic trioxide was assayed for certification as a reductimetric SRM using controlled-current, high-precision coulometry. Coulometry was used for the measurement of acidity in simulated rainwater samples and also in the analysis of high purity acids for use as ion chromatography standards. The one-year tenure of a guest worker from Japan, Dr. Tatsuhiko Tanaka, has resulted in a comprehensive study of current efficiencies at various types of electrodes in relation to the coulometric titration of uranium with electro-generated titanous ion.

Ion chromatography (IC) was well-utilized in the Standard Reference Material program for the determination of sulfur in six types of oil (ranging from 0.14 to 4.5 weight percent sulfur) and in four different coals (ranging from 0.5 to 4.7 weight percent sulfur). These energy-related materials were combusted in a high-pressure oxygen bomb which efficiently converts all sulfur to sulfate. The sulfate is subsequently quantitated by comparison with sulfate standards using the ion chromatograph. Botanical Standard Reference Materials (Pine Needles, Wheat Flour, and Tomato Leaves) were analyzed for sulfur and chlorine by a similar procedure.

In response to a request from another government agency, an improved method for the determination of cyanide ion was developed using ion chromatography with electrochemical detection. The procedure is highly sensitive and selective for cyanide, capable of detecting 1 part per billion in solution. Interference from sulfide or iodide is insignificant unless the concentration of these species greatly exceeds that of cyanide. This method has been applied to assess potential cyanide transport in an industrial setting and could be adapted to the monitoring of air and particulates for trace levels of cyanide.

Chlorine was determined in cadmium sulfide samples by IC to fulfill a request for analytical services. This procedure has been recently published. In a cooperative effort with Catholic University, several leachate samples of glasses and rocks (basalt and granite) were analyzed for anionic content. As part of the NBS-effort in nuclear waste storage research, this Group was responsible for the pH, nitrate, and fluoride measurements in the leach-test protocol study. Fluoride was determined in SRM urine samples using ion-selective electrodes. After a critical evaluation of the analytical work on the reductimetric assay of sodium oxalate (SRM 40h), the certificate was upgraded from provisional to final.

The Acid Rain Program is continuing with an increased emphasis on research leading to the development of reference materials and analytical protocols which will provide traceability to the National Measurement System and assure accurate measurements. A fourth series of Simulated Precipitation Reference Materials (SPRM IV) has been characterized with respect to chemical composition. A program to monitor the stability of SPRM IV, stored in glass and in polyethylene, has been initiated, while the study of SPRM I through SPRM III, stored only in glass, has just recently been completed. Experiments are in progress to assess the long-term stability of dilute acid solutions in polyethylene. Results of these stability projects indicate that the solutions prepared to date that have been stored in glass are not stable with respect to pH, conductance, acidity, alkali metals, or the concentration of several transition elements. Among the recommended changes to be included in the fifth set of samples are the use of polyethylene bottles, and the separation of the major components from the trace elements which must be stored under different conditions for maximum stability. Future research in this program will focus on gaining a better understanding of this complex analytical problem, on establishing practical and theoretically sound protocols for the measurement of pH and acidity, on developing stable reference standards, and on initiating a study of potential source identification based on lead and sulfur isotopic analyses and elemental ratioing.

A high priority project for the coming year will be the certification of pH and pD buffer materials. In addition, proposals have been advanced to study liquid-junction potentials and reference electrodes and to develop the concept of relating the NBS operational pH scale directly to the Faraday through the coupling of coulometry and the hydrogen gas electrode. This research will be conducted in conjunction with the Acid Rain Program and could also be linked to clinical and oceanographic studies. With the aid of an NRC/NBS Postdoctoral Research Associate, voltammetric research will be initiated into the nature and causes of background currents encountered in trace-level amperometric and voltammetric determinations at solid electrodes. Investigations in ion chromatography will concentrate on using the electrochemical detector to enhance selectivity and sensitivity and to augment the types of anions determinable by IC. Foremost on the list are ultra-trace determinations of sulfur as sulfide and analyses of foods for iodide. A workshop, jointly sponsored with the National Committee for Clinical Laboratory Standards will be held next spring to discuss direct potentiometry in blood, with particular regard to sodium measurements.

William F. Koch, Group Leader; E. June Maienthal, George Marinenko,
Kenneth W. Pratt, Jr., Jeffrey W. Stolz, Tatsuhiko Tanaka, David M. Taylor

B. Selected Technical Reports
(Inorganic Analytical Research Division)

1. High-Accuracy pH Measurements (14301)

W. F. Koch, G. Marinenko

The measurement of pH is one of the most common analytical measurements performed both in the field and in laboratories around the world. Its application cross-cuts many disciplines including analytical chemistry, biology, medicine, material science, and nuclear chemistry, as well as a variety of environmental and energy projects. The concept of pH can be described in the strictest theoretical sense; however, the realization of pH (the actual measurement) is possible only in the practical sense and, at present, must be based on quasi-thermodynamic foundations. This in no way detracts from the usefulness of the measurement, but it does make it highly dependent on the standards used to define the pH scale. The operational pH scale used in the United States and in much of the world is defined in terms of a series of standard buffer solutions issued and certified through the Office of Standard Reference Materials.

In order to maintain the standards in this important area of chemical metrology and to expand the utility and applications of pH measurements, a new high accuracy pH/potentiometry facility has been established. Construction of the facility is complete with the acquisition and assembly of the critical elements and instruments. A large controlled-temperature water bath which is used to thermostat the pH measurement cells is operational over the range 0 to 50 °C. The accurate measurement of the bath temperature (±0.01 °C) is obtained through the use of a calibrated quartz thermometer. The quartz thermometer provides the accuracy required for pH research along with the flexibility and convenience that is unobtainable with platinum resistance thermometers.

The emf measurements are made with a calibrated digital voltmeter interfaced to the pH cells and to standard Weston cells through a panel of hermetically-sealed, reed switches. These switches were chosen for their low noise characteristics, low contact resistance, and null leakage current. A digital barometer, calibrated versus the working standard of pressure at NBS, is used to ascertain the pressure of hydrogen gas in the pH measurement cell.

Several configurations of silver/silver chloride reference electrodes have been prepared for use in the hydrogen cells without liquid junctions. These have been tested for physical and chemical stability, reproducibility, temperature coefficient and hysteresis, all parameters critical to accurate pH measurements. Considerable differences have been observed among the potentials of the various types of electrodes, although within-set agreement of the electrodes prepared on a silver wire support is excellent (±0.05 mV). The classical configuration using a platinum wire as the support performed less satisfactorily. Additional research is needed to elucidate these variations. Preliminary pH measurements have been made on solutions of dilute acids and of standard buffer materials. Measurements leading to the certification of renewal SRM pH and pD buffer materials, which are now in short supply, will commence in FY 83. Automation of the facility for routine measurements is anticipated.

In addition, research is proposed to link the existing pH scale directly to a fundamental physical constant, specifically the Faraday. This will be accomplished through the use of high accuracy coulometry to determine, on an absolute basis, the hydrogen ion content of dilute solutions of highly purified mineral acids. The activity coefficients of these simple solutions can be calculated from thermodynamic considerations. These solutions will then be systematically compared with the primary standard buffer materials which now serve to maintain the NBS practical pH scale. A thorough examination of reference electrodes and liquid junction potentials will be a necessary part of this endeavor.

Future applications of this new pH facility will include the preparation of accurate pH standards to assure quality in analytical measurements and the expansion of the utility of the NBS pH scale as both a practical and a theoretical analytical tool. An important goal of this program is to produce and distribute pH standards which simulate the varying matrices and ionic strengths encountered in solutions such as acidic precipitation, body fluids, and seawater.

2. Resonance Ionization Mass Spectrometry of Vanadium, Molybdenum, and Rhenium (51108)

J. D. Fassett, F. E. Lytle, L. J. Moore, J. C. Travis

Resonance ionization mass spectrometry (RIMS) is an innovative technique combining mass spectrometry with laser photoionization to selectively and sensitively produce ions from a gas phase reservoir of atoms. The technique exploits both the limited bandwidth and intense photon flux inherent in laser radiation. By tuning the laser to a discrete electronic transition of an element where the photon absorption cross section is increased many fold (a resonant process), the ionization probability becomes similary increased due to the stepwise absorption of subsequent photons. This particular technique differs from other spectroscopic techniques in that the absorption or emission of photons is not directly measured, only the ions that are produced are measured. Thus, there exists a combined elemental selectivity (due to the ionization) and isotopic selectivity in the measurement process. To date, resonance ionization has been studied predominantly in ionization chambers without mass selected measurement and only for a limited number of elements (potassium and a few rare earth elements), although possible schemes for resonance ionization of a majority of the elements in the periodic table have been published by other researchers. As part of a multiyear competence research program in ionization mechanisms and ion structures, a RIMS system has been built (described in another technical report), and resonance ionization of the elements V, Mo, and Re has been demonstrated.

The formation of atomic ions using resonance ionization requires a source of neutral atoms which can be supplied by either single or multiple filament thermal ion sources used in conventional stable isotope mass spectrometry. Langmuir vaporization of salts or metals deposited on a filament surface will produce a gas phase reservoir of neutral atoms under the appropriate conditions. One of the prime motives for the development of RIMS was the investigation of the thermal ionization process to understand the mechanisms in Langmuir vaporization and ion formation. The results to date indicate that Langmuir vaporization is ideally matched with RIMS and valuable information in both processes will be gained.

Three elements, V, Mo, and Re, whose ionization potentials are 6.7, 7.1, and 7.9 eV, respectively, have been initially investigated by RIMS. The coherent radiation provided by a Nd-YAG laser pumping a tunable dye laser with a frequency-doubled output was used to access resonance levels of the elements that were vaporized from the modified thermal ion source of a magnetic sector mass spectrometer. Molybdenum atoms were produced from molybdic acid reduced under hydrogen on the rhenium substrate; vanadium atoms were produced from $VOCl_3$ dried on the rhenium substrate; and rhenium atoms were produced directly from one rhenium filament substrate. The microgram quantities of V or Mo produced steady state reservoirs of gas phase atoms which were not depleted in the experiment at operational temperatures of 1275 °C and 1590 °C, respectively. Detection and measurement of the mass selected ions were accomplished with a 17-stage electron multiplier whose amplifed output was coupled to a boxcar averager synchronized to the laser pulse and delayed for the appropriate time-of-flight of the ion.

The spectroscopy of ionization has proved to be extremely interesting. Three resonance lines of Mo (3002.211, 3112.12, 3132.59 Å) and two resonance lines each of Re (2976.29, 299.31 Å) and V (2942.35, 2943.20 Å) were investigated. The spectral structure varied considerably among the elements and includes the appearance of non-resonant peaks, non-resonant background, and differing resonant peak shapes, intensities, and laser power dependencies. Figure 12 illustrates part of the Mo spectrum. The two non-resonance lines and shoulder to the 3132.59 Å resonance line have yet to be satisfactorily explained. The sharpest resonance line observed to date has been the 2976.29 Å line of Re equal to 0.3 Å at half maximum.

Saturation of the ionization signal has been observed at readily attainable laser powers, from which it can be inferred that ionization efficiencies are 100 percent in the laser focal volume exposed to ion source extraction optics. These preliminary results also indicate that there exists a trade off that must be made between optical selectivity and sensitivity in this experimental arrangement of RIMS because of the quadratic nature of 2-photon non-resonance ionization background caused by the saturation broadening of optical transitions at laser powers required for 100 percent ionization.

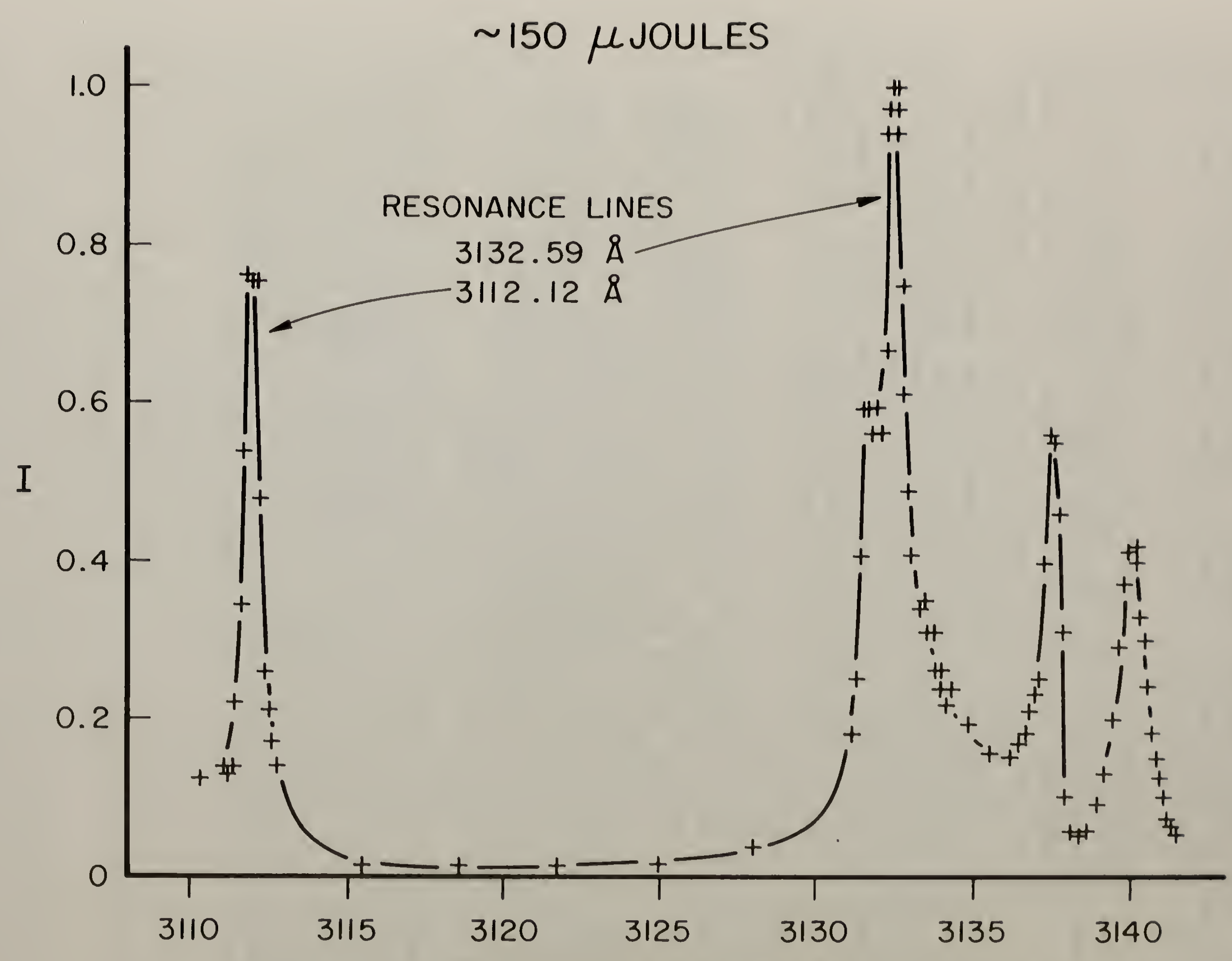

Figure 12. $^{98}Mo^{+}$ intensity versus laser wavelegth.

3. Depth Profiling of Bismuth in Silicon and Tin with Low-Energy Neutrons (51109)

R. G. Downing, R. F. Fleming

A depth profiling facility similar to the one at the Institute Laue-Langevin Research reactor in Grenoble, France [1] is currently being developed at the National Bureau of Standards Research Reactor. Profiling is accomplished by evaluating the residual energy of those particles escaping the parent matrix due to *in situ* nuclear reactions induced by low-energy neutrons. Concentrations and depth distributions are then made having *a priori* knowledge of the matrices' stopping function and counting statistics. Since the primary neutron beam imparts a negligible amount of energy in this process, this technique offers the attractive possibility of causing minimal direct damage to samples which have the appropriate isotopic species.

Of the species traceable in the above manner, bismuth is of particular interest in that it yields delayed alpha particle emission upon activation. All other known species are prompt particle emitters upon activation and therefore are confined to analyses only during the irradiation process on the reactor beam line. Bismuth's unique property thereby allows the activated sample to be conveniently removed to a remote counting site for profiling.

Parallel measurements have been conducted on bismuth distributions by means of neutron depth profiling (NDP) and secondary ion mass spectroscopy (SIMS) to demonstrate the synergistic possibilities of combining depth profiling techniques. As an example, Figure 13 shows the bismuth distribution in a 30 keV bismuth implant in silicon [2] (dose = $4.4 \pm 0.1 \times 10^{15}$ atoms/cm^2) determined by SIMS and the corresponding energy spectrum as measured by NDP. In this particular case, the implant is shallow enough that essentially no energy loss occurs for the alpha particle traveling in the silicon. As a result, the width of the energy distribution measured by NDP is determined by the spectrometer response function. Knowing the total dose of bismuth in the sample, the integrated counts in the NDP spectrum can be used to determine a calibration factor for the system.

A second bismuth-containing sample was then analyzed. This sample consisted of an approximately 2.5 µm-thick bismuth layer evaporated on a tin substrate, heated in air at 150 °C and rapidly cooled. A SIMS depth profile of the resulting layer revealed mixing of the bismuth and tin, with an apparent surface peak in both bismuth and tin overlying a layer of bismuth-tin alloy of homogeneous composition. Obviously, both tin and bismuth cannot increase at the surface. The apparent enhancement is at least partially due to matrix effects on the secondary-ion intensities. A NDP profile of the same layer confirmed the existence of a real surface bismuth peak as well as the homogeneous subsurface layer. The bismuth calibration factor obtained from the bismuth-silicon implant can be used to derive the number of bismuth atoms per unit volume in the homogeneous layer. Assuming the density of this layer to be approximately that of tin, the major component, and determining the number of tin atoms per unit volume by difference, yielded a Bi/Sn atom ratio of 0.14 in the homogeneous layer. This ratio corresponds very well with the solubility of bismuth in tin at the temperature of heat treatment. A SIMS

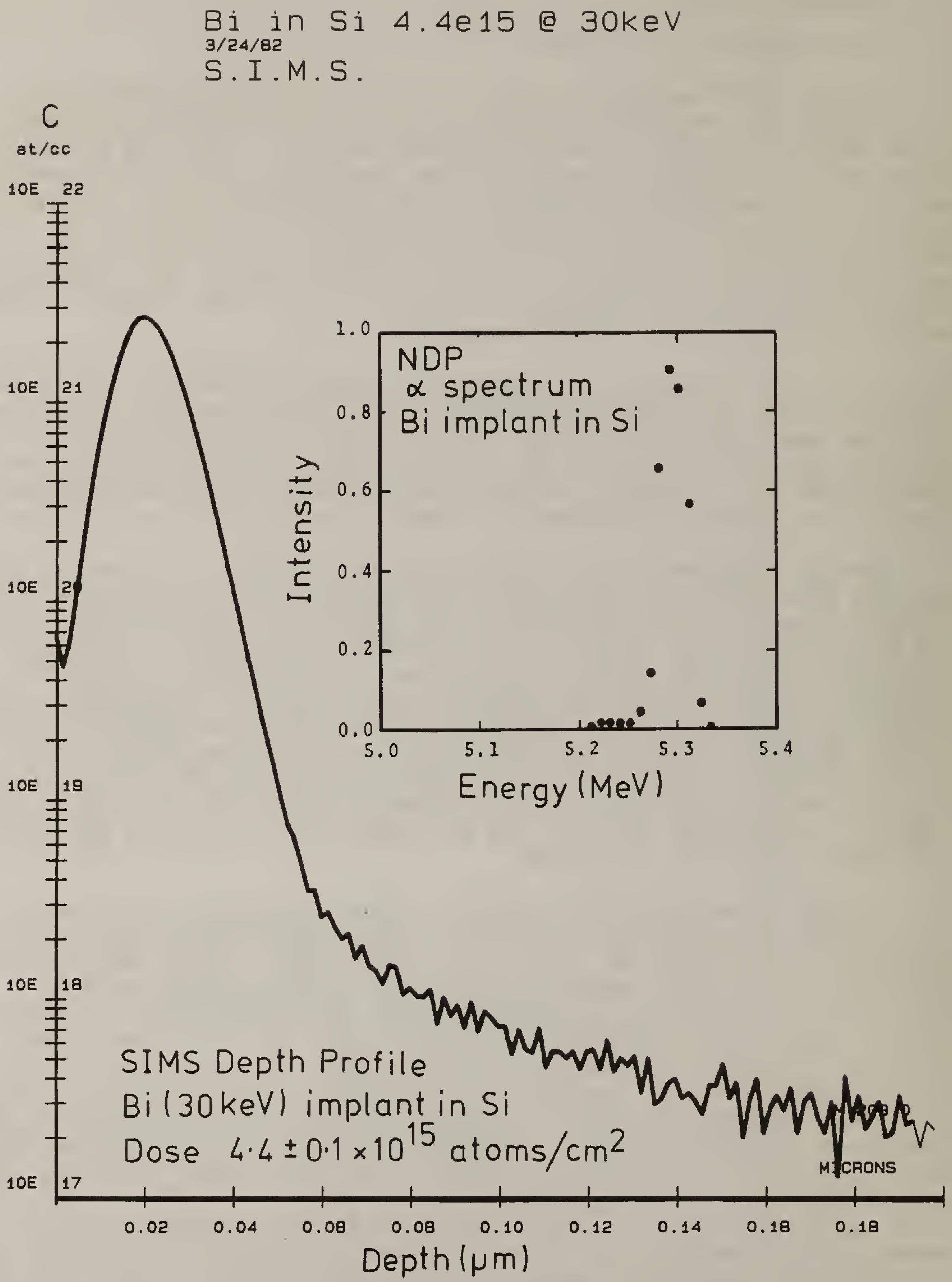

Figure 13. Depth distribution of bismuth implanted at 30 keV into silicon, as determined by SIMS.
Inset: corresponding profile as measured by NDP.

sensitivity factor SBi/Sn = (IBi/CBi)/(ISn/CSn) can thus be calculated from this NDP atom ratio (CBi/CSn) and the SIMS intensities (IBi/ISn) measured in the homogeneous layer. A value for SBi/Sn of 2.9×10^{-2} can be determined from these calculations. Finally, by using this SIMS sensitivity factor, the initial portion of the SIMS depth profile can be corrected to yield an apparent concentration ratio axis, as shown in Figure 14.

This example demonstrates the potential for synergistic interaction of neutron profiling with the more commonly available methods for depth profiling. Although at present the NDP technique is limited in application to elements of adequate sensitivity, refinement of the charged particle spectrometer to include coincidence counting may extend the method to additional systems.

References

[1] Biersack, J. P., Fink, D., Henkelmann, R. A., and Muller, K., "The Use of Neutron Induced Reactions for Light Element Profiling and Lattice Localization," Nucl. Inst. Meth., 149, 93 (1978).

[2] The Bi-Si sample was kindly supplied by Dr. John Baglin of IBM (Yorktown Heights); the dose was derived from a round-robin study by Rutherford backscattering (Baglin, unpublished results).

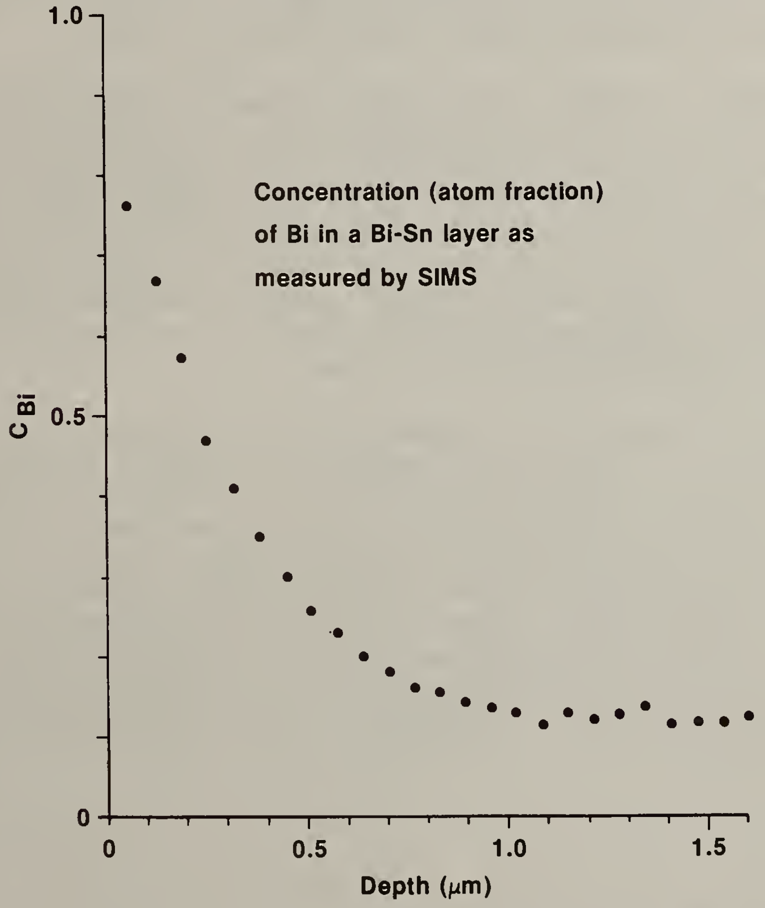

Figure 14. SIMS depth profile of bismuth in the bismuth-tin alloy layer with sensitivity factor corrections applied to derive a concentration axis.

4. Determination of Provenience of Artifacts with Lead Isotope Ratio Measurements (11310)

I. L. Barnes, E. C. Deal

For more than ten years, the Mass Spectrometry Group has collaborated with a number of museums in providing information concerning the possible provenience of artifacts through the measurement of lead isotopic ratios. Useful information comes from the fact that each lead deposit in the world has a unique set of lead isotopic ratios which are preserved in the statue, coin, glass vessel, etc. made with the smallest amounts of lead. Because the isotopic differences are usually very small, a high accuracy measurement procedure like the one developed at NBS is required.

The demand for this measurement information has increased to the point where the services of a full time analytical chemist are required in order to meet minimum needs. Fortunately, a grant from the Smithsonian was made available to the Freer Gallery to support a Freer employee as a guest worker at NBS for two years. Although the first year has been largely devoted to training in the chemical and mass spectrometric procedures necessary for high accuracy measurements, useful results have been obtained. The results from analyses of samples provided by R. Brill of the Corning Museum of Glass, P. Meyer of the Metropolitan Museum of Art, and T. Chase of the Freer Gallery, are shown, along with a summary of previous data, in the following figures.

The ellipses shown in Figure 15 have been defined by the analyses of nearly 1,000 ores or objects of known Egyptian, Greek (L), English (E), Spanish (S), or Italian area (X) origin. The two data points just to the left of the "L" region were obtained from metallic objects taken from a ship wreck discovered off the coast of Greece and the results are consistent with a Turkish origin. The data point within the "E" region is from a piece of yellow, opaque glass of "European or Chinese" origin. The data point within the "L" region is from a glass bead found in Japan and believed to be of Chinese origin and is discussed generally below.

Figures 16 and 17 are extensions (same scale) of the upper right and lower left of Figure 15. It should be noted that the data from these samples tend to group into three clusters, two to the upper right and one to the extreme lower left, of the expanded graph. This is consistent with the small amount of previous data from samples of presumed Chinese origin. It may be possible in the future to determine the location of these three geologically different regions of manufacture if samples of native ores could be obtained. To date, only a very few galenas have been obtained. The few samples analyzed of known forgeries of Chinese objects have yielded data which falls in or near the "L" or "S" regions. At present, the significance of this information is not clear.

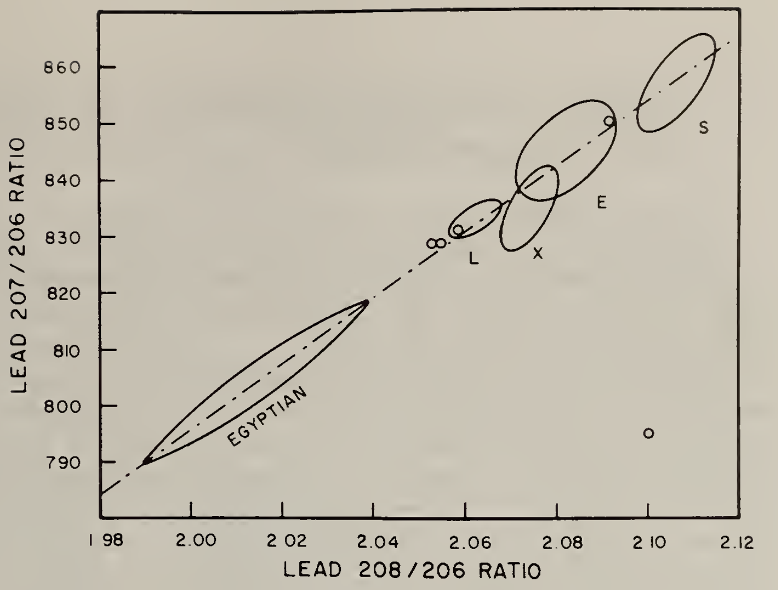

Figure 15.

Plot of lead 207/206 versus lead 208/206 ratios. Ellipses have been defined by a large number of previous samples.

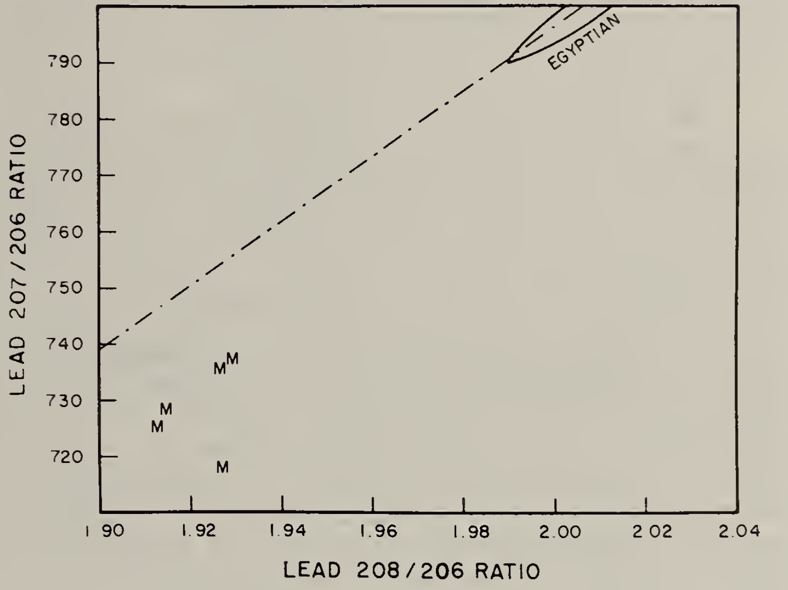

Figure 16.

Extension of the lower left of Figure 15 (same scale). Data points (M) are from Chinese bronzes from the Metropolitan Museum of Art.

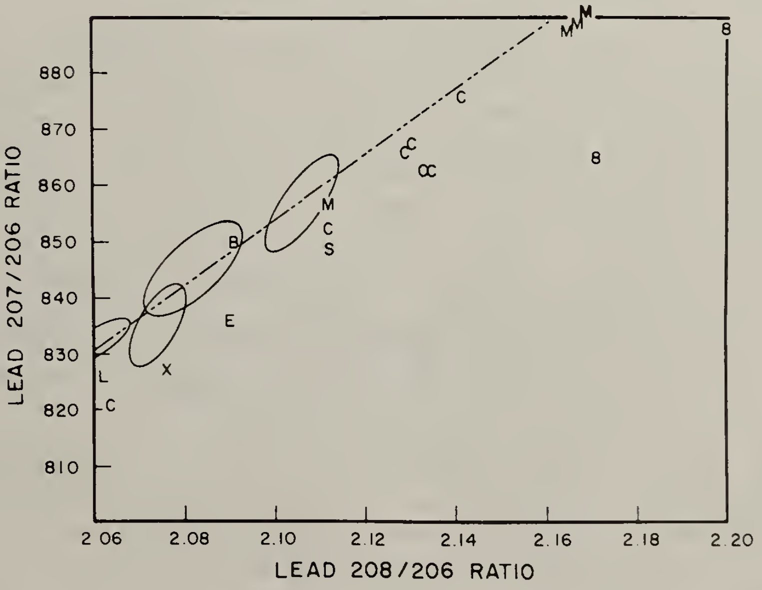

Figure 17.

Extension of the upper right of Figure 15 (same scale). Data points are from samples of Chinese glass and bronze objects from (B) the Corning Museum of Glass, (C) the Freer Gallery of Art, and (M) the Metropolitan Museum of Art.

5. Treatment of Sources of Variability in the Inductively Coupled Plasma (ICP) Technique (14625)

R. L. Watters, Jr.

The Inductively Coupled Plasma (ICP) technique has been applied to certification as well as homogeneity assessment of various elements in Standard Reference Materials (SRM's). For an element being determined at a concentration well above its detection limit, the ICP technique can achieve short-term precision of less than one percent relative standard deviation (RSD). Under such conditions, the principal source of variability is random nebulizer noise. However, for homogeneity assessment, duplicate analyses on several batches of material are required to provide the analyst with the number of degrees of freedom necessary to make a meaningful statement concerning the between batch variance. Unfortunately, when the number of samples is increased, the corresponding increase in the time of analysis usually allows other sources of variability, such as nebulizer drift, to affect the quality of the results. Two approaches have been used to address this problem.

The first approach involves sample preparation procedures which reduce the amount of non-random nebulizer variability. It has been found that when samples of an organic matrix are wet-ashed using perchloric acid, the resulting solutions cause appreciable nebulizer pressure drift (approximately one psi). During simultaneous multielement analysis, a corresponding drift in element net intensities has been observed. The degree of intensity drift for a given element depends on its optimum observation point in the plasma flame relative to the compromise observation point chosen for all elements. An alternate sample digestion procedure has been used for the ICP certification analysis of SRM 1084 and 1085, Wear Metals in Oil. Ten elements were determined in aqueous solutions of the two materials following a sealed-tube dissolution using hydrochloric and nitric acids. In this particular case, up to 0.5 g of oil can be digested with the resulting solution containing two percent HNO_3 by volume. For the samples prepared to date, no detectable pressure drift has been observed during long-term nebulization.

The second approach to isolating variability associated with sample batches was to develop software for on-line data analysis of variance (ANOVA). This development was possible only after the completion of the communication network and protocols mentioned in last year's annual report. A modification to the commercial ICP software package was also required because the analysis data are stored in a format suitable only for report writing. The output subroutine of a report writing program was modified to write sample identification numbers and associated analytical data into a separate ASCII file which can be accessed by other computers. This file can be transferred to the NBS main computer for analysis by the OMNITAB software or to a Z-80 microcomputer for analysis by BASIC 80 software. For SRM homogeneity studies, the file can be transferred to the microcomputer for an analysis of variance of hierarchic data with three sources of variation. The first application of this approach was in the determination of magnesium in duplicate samples from 11 bottles of SRM 1549, Powdered Milk. The samples were run in random order using four instrumental integrations for each. Estimates for variance in (1) SRM bottles, (2) sample preparation and instrumental drift, and (3) instrument integrations were calculated in a total of five minutes after reading the data from the minicomputer disc. An average value for each SRM bottle and the standard ANOVA, Table 5, is printed on one page for each element determined.

Using these two approaches, one source of variance in the sample introduction step of the ICP technique can be significantly reduced and estimates of three sources of variance in the entire analytical scheme can be calculated.

Table 5. ICP Results for Mg in Powdered Milk.
(μg/g)

SRM Bottle	Sample 1	Sample 2
12-2	1210.00	1201.12
06-2	1185.63	1213.25
10-2	1177.67	1247.55
01-1	1265.73	1177.13
11-1	1186.38	1248.90
03-2	1256.65	1224.13
07-1	1202.28	1240.50
02-1	1213.70	1168.35
09-2	1186.30	1204.35
08-1	1204.92	1210.07
04-1	1196.67	1206.52

Analysis of Variance for Element Mg

Source of Variation	Sum of Squares	D.F.	Mean Square
Between Groups (SRM Bottles)	16246.843	10	1624.680
Between Samples Within Groups	45017.498	11	4092.500
Within Samples	12731.806	66	192.906
Total	73996.200	87	

The mean squares estimate the following:

$$1624.680 = V(0) + 4\ V(1) + 8\ V(2)$$

$$4092.500 = V(0) + 4\ V(1)$$

$$192.906 = V(0)$$

Where V(2) = SRM-Bottle-to-SRM-Bottle Variance

V(1) = Sample-to-Sample Variance and Instrument Drift

V(0) = Variance Due to Instrumental Integrations

The estimates are:

V(2) = -308 (essentially zero)

V(1) = 975

V(0) = 193

6. Effect of Natural Isotopic Variability on Accurate Determination of Sulfur by Neutron Activation Analysis (11310)

R. F. Fleming, R. M. Lindstrom

The instrumental neutron activation analysis of sulfur depends on the activity of ^{37}S produced from the ^{36}S isotope which has a natural abundance of approximately 0.02 percent. Wide variations in the isotopic ratios of naturally occurring sulfur were first demonstrated by the McMaster group using mass spectrometric techniques and has since been documented for thousands of samples. The effects on accurate activation analysis of any isotopic fractionation are usually negligible for reactions on isotopes of major abundance. However, for isotopes of minor abundance, such as ^{36}S, accurate activation analysis requires that either the isotopic compositions of both the samples and standards be the same or that the compositions of both be explicitly known.

Although careful mass spectrometry can determine the $^{36}S/^{32}S$ ratio directly, the isotopic fractionation of ^{34}S is typically measured and expressed as

$$\delta^{34}S = \left[\frac{(^{34}S/^{32}S)\ \text{sample}}{(^{34}S/^{32}S)\ \text{standard}} - 1\right] \times 1000$$

Meteoritic troilite (FeS) is the usual standard ($\delta^{34}S = 0$) since it is believed to reflect the mean solar system abundance and has not been fractionated. Seawater sulfur is uniformly enriched in ^{34}S by 20 parts per thousand ($\delta^{34}S = +20$ o/oo). Volcanic sulfur has a range of $\delta^{34}S$ from -10 to +10 o/oo while the S^{34} in coal and petroleum ranges from -30 to +30 o/oo. The range of published values for $\delta^{34}S$ is from -53.1 o/oo for a Texas marcasite (FeS_2) to +86.7 o/oo for a barite ($BaSO_4$) from the Japan Sea. Using the theoretical relation for the fractionation of sulfur isotopes, one can estimate the spread in the abundance of naturally occurring ^{36}S:

$$\ln(1+\delta^{36}S) = (1.90 \pm 0.01)\ln(1+\delta^{34}S)$$

$$\ln(1+\delta^{33}S) = (1.94 \pm 0.01)^{-1}\ln(1+\delta^{34}S)$$

This model predicts a maximum difference of 29 percent in the ^{37}S specific activity of sulfur samples irradiated under the same conditions. The $\delta^{34}S$ spread for coal and petroleum is large enough to limit the accuracy of sulfur determination to ±15 percent, regardless of the precision of the measurement. Other nuclear techniques which depend on the properties of the major isotope ^{32}S, such as prompt-gamma neutron capture activation analysis (PGAA) or fast-neutron activation followed by counting of ^{32}P, are only slightly affected by isotopic fractionation.

In this work, the systematic error from the isotopic variability is demonstrated by determining the ^{37}S counting rate per unit mass of sulfur produced after irradiation of five $\delta^{34}S$ standards from McMaster University (the SL-277 series) as well as a galena, a barite, and an elemental sulfur standard. Several other sulfurs of unknown isotopic composition including the NBS SRM 371g were also run. The McMaster samples were converted from

Ag_2S to H_2S with HCl, and from H_2S to S with I_2, followed by purification of the product. The volcanic samples and some of the laboratory sulfurs were purified by recrystallization. The samples, weighing from 12 to 90 mg, were irradiated in the NBS reactor, and after a fixed decay time, the 3103 keV gamma ray was counted with a germanium detector. Zinc flux monitors were run with each irradiation to assure the constancy of the neutron flux, and small corrections were made for dead-time and pulse pileup.

There is a six percent difference in response among sulfurs from commercial suppliers, perhaps a three percent difference among the volcanic sulfurs, and an apparent $\delta^{34}S = 0$ for the SRM sulfur. The results for the standards are plotted against $\delta^{34}S$ in Figure 18, with each data point representing the average of at least two measurements and the error bars representing counting statistics (1σ) only. The solid line is the predicted curve based on equation two, normalized to the measured activity for sample SL-277-1.

In summary, it has been demonstrated that the known isotopic variability of ^{36}S results in a corresponding inaccuracy in the measurement of sulfur by neutron activation and that this effect is well predicted by the theory. The worst-case limit on the measurement accuracy is ±29 percent; however, this uncertainty can be halved if one uses a standard of known isotopic composition.

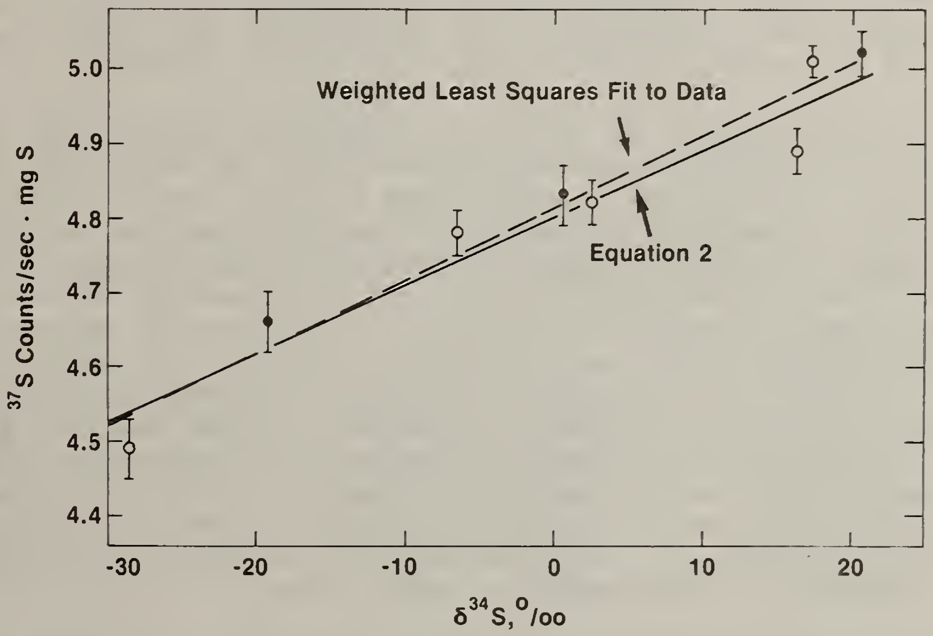

Figure 18. Sulfur-37 specific counting rate versus ^{34}S variation in parts per thousand for the eight isotopic standards.

7. Application of ID/MS to the Determination of Sulfur in Biological and Environmental Standards (14307)

W. R. Kelly, P. J. Paulsen

The new procedure developed last year for the determination of sulfur using thermal ionization mass spectrometry has been further investigated and applied to a variety of materials with sulfur concentrations ranging from 3 ppm to 4.5 percent. In addition, this technique has been applied to the precise measurement of the sulfur isotopic composition of the above materials. Because the sulfur isotopic composition is variable in nature as a result of mass dependent fractionation, it is necessary to measure the composition in each sample in order to calculate accurately the sulfur concentration. The isotopic composition of sulfur is approximately 95 percent ^{32}S, 0.75 percent ^{33}S, 4.2 percent ^{34}S, and 0.02 percent ^{36}S.

To determine sulfur concentration, appropriate quantities of sample, ^{34}S enriched spike, along with nitric and hydrochloric acids are equilibrated in a sealed pyrex tube (modified Carius tube) to prevent loss of volatile sulfur compounds. The oxidized sulfur ($SO_4^=$) that is formed is subsequently reduced to H_2S and precipitated as As_2S_3. The As_2S_3 is dissolved in an NH_3-As(+3) solution to yield an As/S atom ratio of two and a sulfur concentration of 100 µg S/mL. About 1.5 µg S is loaded on a rhenium filament with silica gel. Sulfur isotopic ratios are measured as the AsS^+ ion. Since As is mononuclidic, the ion intensities at masses 107, 108, 109, and 111 from ^{75}AsS are directly proportional to the abundances of sulfur 32, 33, 34, and 36.

The results obtained for sulfur in freeze dried Bovine Liver (SRM 1577a and 1577b) illustrate the high accuracy and precision that can be obtained by this technique. Two batches (a and b) were prepared from a single lot of bovine liver. Six bottles from each batch were analyzed and the data are given in Table 6. The "a" samples were packaged material whereas the "b" samples were taken from different barrels of the unpackaged material. Replicate analyses of both materials differ by only one to three units in the third place indicating both good measurement precision and sample homogeneity. The mean sulfur values for the "a" and "b" materials are indistinguishable even though there was considerable difference in weight loss during vacuum drying. This demonstrates that the drying procedure reduces all samples to the same weight basis and indicates that improper drying could cause an inaccuracy of several percent. The total spread in the sulfur contents within the "a" and "b" materials is 0.25 percent and 0.52 percent relative and indicate the degree of homogeneity in sulfur content.

In Table 7 are listed the high level biological samples that have been certified. Both the sulfur concentration and the $^{32}S/^{34}S$ ratios are given. The larger uncertainties of the coal concentrations reflect the larger spread in the replicate values. All of these organic materials have $^{32}S/^{34}S$ ratios that are different. The coal SRM's show a range of 1.6 percent in their $^{32}S/^{34}S$ ratios which is a factor of 10 greater than the typical measurement imprecision. The variation of the $^{32}S/^{34}S$ ratio in nature has been used to trace the origin and mode of formation of rocks, minerals, ore deposits, and fossil fuel deposits. Another important use, which has only recently been explored, is the use of the differences in $^{32}S/^{34}S$ to identify sources of sulfur compounds in both wet and dry deposition. It may prove possible to distinguish between natural and anthropogenic sources of sulfur in specific locations.

Table 6. Sulfur Concentration in SRM's 1577a and 1577b, Bovine Liver as Determined by Thermal Ionization Mass Spectrometry.*

Bottle #	S%	Wt. Loss (%)
1	0.7836	1.50
2	0.7852	1.54
3	0.7848	1.49
4	0.7856	1.50
5	0.7842	1.40
6	0.7837	1.63
Mean	0.7845	
Uncertainty	±0.0046	
3d	0.7863	3.88
4c	0.7846	4.39
4d	0.7841	6.26
5d	0.7851	4.40
7d	0.7851	5.39
9d	0.7822	5.21
Mean	0.7846	
Uncertainty	±0.0061	

Table 7. Sulfur Concentrations and $^{32}S/^{34}S$ Ratios in Biological Materials.*

	%S	$^{32}S/^{34}S$
SRM 1572, Citrus Leaves	0.4066 ± 0.0022	22.63
SRM 1577a, Bovine Liver	0.7845 ± 0.0046	22.56
SRM 1577b, Bovine Liver	0.7846 ± 0.0061	22.56
SRM 2682, Coal	0.4934 ± 0.0092	22.70
SRM 2683, Coal	1.896 ± 0.033	22.36
SRM 2684, Coal	3.076 ± 0.090	22.73
SRM 2685, Coal	4.761 ± 0.188	22.55

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*In both Tables 6 and 7, the uncertainty for an individual determination was calculated as the linear sum of the 95 percent confidence interval (ts) for the six analyses, the 95 percent confidence interval (ts) for ten spike calibration mixes, and the uncertainty in the blank. This last quantity was assumed to be equal to the largest blank observed. In Table 7, the measured isotopic ratios have not been corrected for instrumental mass fractionation and thus are not absolute ratios.

8. Development of a Laser Mass Spectrometry Laboratory (51108)

J. D. Fassett, L. J. Moore, J. C. Travis

The objectives of the research in laser mass spectrometry are to develop highly sensitive and selective atom counting technology and to investigate the vaporization, isotopic discrimination, and ionization behavior of inorganic compounds in thermal ion sources. The measurement impetus for this research derives from projected sensitivities and selectivities for the formation and measurement of ions. Atomic ionization sensitivity and selectivity are available using tunable laser radiation for resonance ionization. A capability for selective isotopic measurements is being developed using laser induced ion fluorescence for mass-selected high velocity ions.

The first phase of the development of this laboratory has been completed (Figure 19). Laser and mass spectrometry systems were selected to provide maximum flexibility to access all but the most difficult atomic ionization potentials in the periodic table. A 700 mJ pulsed Nd-YAG laser, which pumps a tunable dye laser coupled to a frequency doubler, generates highly coherent wavelengths down to the near UV ($\sim$260 nm). The output of the pulsed laser system can be directed to the ionization region of a time-of-flight or a magnetic sector mass spectrometer to permit efficient and selective removal of electrons using the principles of resonance ionization. A second laser system consists of a continuous wave (CW) argon ion laser used to pump a scanning single mode tunable dye laser. The output of the CW system can also be routed to the ionization region of either mass spectrometer or to the detector region of the magnetic sector instrument. Continuous wave radiation can be used to produce ions directly or to selectively excite electrons to Rydberg states prior to electrostatic stripping of the electron. The single mode CW output can also be used to produce laser induced ion fluorescence (LIIF) in mass-selected ions and to study atomic fluorescence of neutral species in thermal vapor plumes.

A real time diagnostic capability has been developed to probe thermal vapors using the laser time-of-flight mass spectrometer combination. A complete mass spectrum can be produced for each laser or electron impact pulse using a 200 MHz transient digitizer with 4096 5-nsec channels. Successive spectra can be computed, averaged, recorded, and sequentially displayed. This capability will be used to characterize complex thermal vapors and to evalute the feasibility of inorganic valence state speciation. The resonance ionization mass spectrometry (RIMS) of Mo, Re, and V has been observed and is described in another technical report.

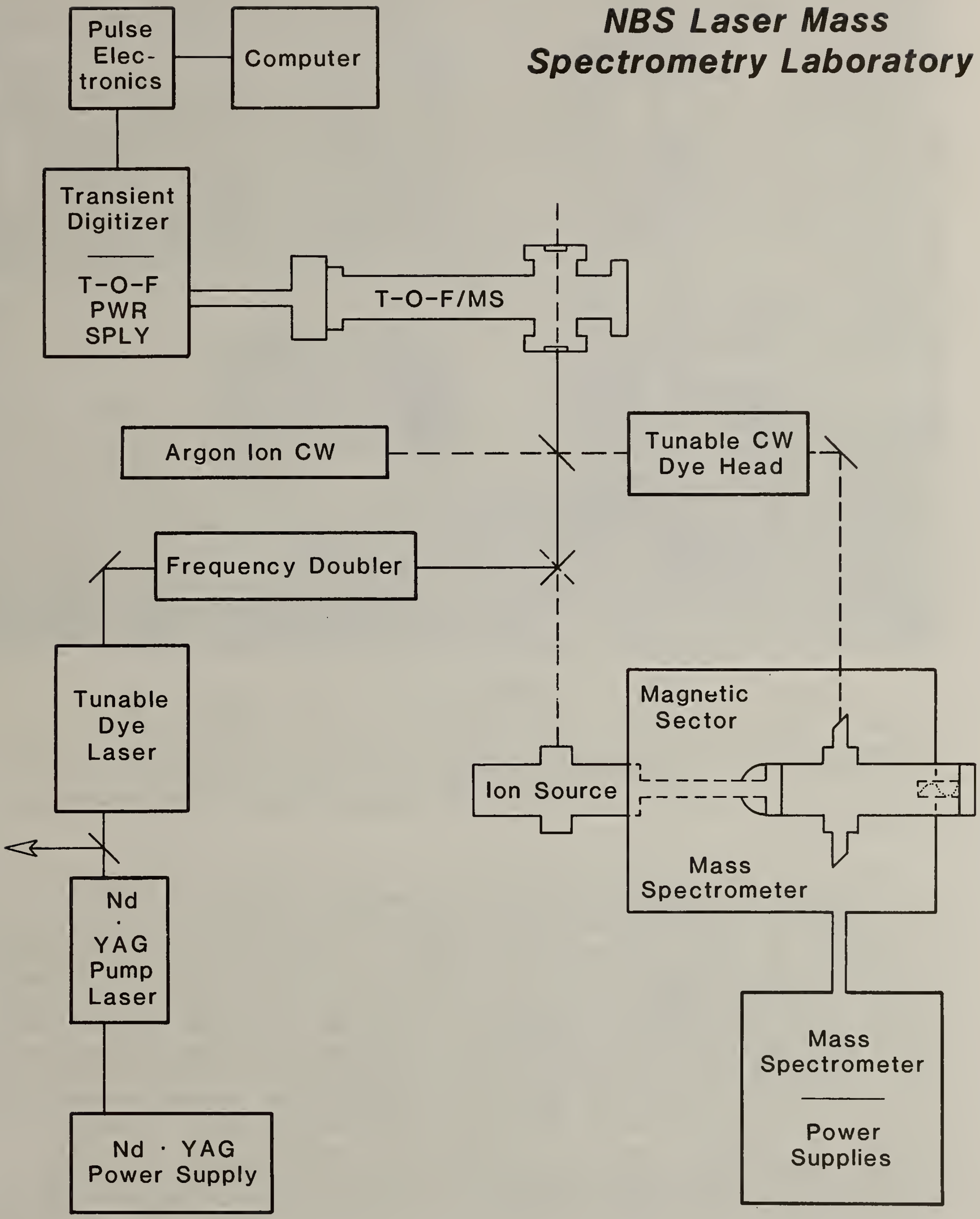

Figure 19. NBS laser mass spectrometry laboratory.

9. Design and Construction of a Modern Facility for the Production of Ultrapure Reagents (11310)

E. S. Beary, J. R. Moody

Two previous acid facilities, set up in existing modular laboratories, were unsuccessful due to corrosion, poor ventilation, and potential safety problems. The new laboratory was specifically designed to overcome all previous difficulties and provide a permanent safe laboratory for purified acid preparation. The laboratory has been operational for nearly a year, and it is now possible to compare theoretical operating parameters with actual experience. Two basic requirements governed the design of the laboratory: (1) the provision of high volume, single pass, class 100 supply air with an all plastic exhaust sytem and (2) careful control of the balance of air flows; removing acid fumes at their source without either introducing fumes into the laboratory or permitting fumes to escape the area outside the laboratory.

Within the laboratory, the primary concern was to eliminate those materials which contained metals (a source of contamination) or which could be attacked by fumes or by contact with acids. This latter factor largely determines the useful life of the laboratory and, as learned from previous experience, compromise usually results in failure of the component. In general, the first year's experience has indicated that the design principles and choice of materials were valid. Most of the relatively minor problems have been related to plumbing (leaks) or plastic ductwork (leaking joints). The flooring should have been PVC but reasonably priced flooring made from PVC is not available in the U.S. The substitute material, a proprietary formulation, is functional but difficult to keep clean.

The potential for spills or accidents is in itself greatly reduced because of laboratory design. All acid spills would be automatically contained and conducted to a drain. Spills in the distillation module itself are automatically diluted with water. Because of the improved and precise control of air supply and fume exhaust, no free acid odor can be detected in the laboratory.

The new laboratory, shown in Figure 20, is presently operating at full capacity with 13 stills installed for the continuous production of five mineral acids and the occasional purification of a sixth material such as HBr, HOAc or any one of a number of solvents. In addition, the facility has storage capacity for about 250 L of purified acid and about 100 clean Teflon bottles. An exhaust hood with non-recirculating air is in use for the cleaning of Teflon bottles and labware for trace metal analyses in an effort to save the clean laboratory from further corrosion due to uncontrolled acid fumes. By any measure of product quality, product quantity, or efficiency of production, all expectations have been achieved. The lifetime of this laboratory will surely be many times longer than previous efforts have produced. In addition, there is a significantly improved level of safety for those within the environment without any sacrifice in terms of quality of product or utility of the laboratory.

Figure 20. Ultrapure Reagent Laboratory.

10. Improved Procedure for the Determination of Cyanide by Ion Chromatography with Electrochemical Detection (14215)

W. F. Koch

The use of cyanide is widespread and vital to industries involved in such commercially important operations as electroplating, extracting precious metals, chelating metals, case hardening of steels, and fumigating orchards. The extreme toxicity of cyanide requires that its use be strictly controlled and that proper monitoring be in effect to guard against environmental contamination. To address the question of trace level contamination and prompted by a request for assistance by another government agency, a highly sensitive and selective method for the determination of cyanide has been developed. The method employs ion chromatography with electrochemical detection (IC/EC) and determines free, uncomplexed cyanide ion in aqueous solution.

Sample preparation for this procedure is minimal. Aqueous samples may be analyzed directly while dust and particulate samples need only to be extracted into an aqueous solution to dissolve the soluble cyanide. This is most conveniently effected through agitation in an ultra-sonic bath. The solution must be filtered before analysis in order to avoid fouling of the chromatographic columns. Commercially-available anion exchange columns with high ion-exclusion properties are used to separate the cyanide ion from other anions. A suppressor column is not required in this application of ion chromatography. The eluent contains 15 mmol/L ethylenediamine, 5 mmol/L sodium hydroxide, 2.5 mmol/L borax, and 1.0 mmol/L sodium carbonate. It is pumped through the IC/EC system at the rate of 4 mL/min.

The detection system uses a commercially available three electrode potentiostat and a flow-through cell. The working electrode is a silver rod; the reference is a silver/silver chloride electrode; and the counter electrode is platinum. Samples and standards are injected into the IC/EC system by means of a 50 μL sample loop. Under these conditions, the peak retention time for cyanide is approximately five minutes. The amperometric signal at the peak is proportional to cyanide concentration with a minimum detection limit of one part per billion (ppb) and with linearity from this level to one part per million (ppm). The range can be extended to higher levels with smaller sample loops or by dilution of the sample.

Due to the excellent chromatographic resolution of sulfide, iodide, and cyanide, no serious interference exists unless the concentration of iodide or sulfide greatly exceeds that of cyanide. This represents a considerable advantage over the ion-selective electrode and the colorimetric procedures commonly used in cyanide analyses, which are severely biased by the presence of trace quantities of sulfide and to a lesser extent of iodide. Furthermore, the IC/EC procedure extends the minimum detection limit at least one order of magnitude below that attainable by the commonly used procedures.

With this improved method for the rapid determination of cyanide, the means are available to assess potential cyanide transport in those cases where health and environment are major concerns. Research is continuing to assess the precision and accuracy of this procedure and to expand its applications.

11. Direct Determination of Calcium in Urine Using a Thermally-Regulated D.C. Plasma-Echelle Spectrometer (14306)

C. G. Blundell, M. S. Epstein

Wavelength drift and order drift, both thermally-induced, were two major problems that had been encountered in this laboratory in the use of the dc plasma/echelle spectrometer. The dc plasma source is directly mounted on the aluminum baseplate of the echelle spectrometer and the heat generated by the plasma raised the temperature of the baseplate several degrees Celsius during eight hours. The resulting drift severely limited the precision and accuracy obtainable with the plasma spectrometer and made it necessary to develop a temperature stabilization system.

Thermal regulation is performed by a temperature sensor/controller which monitors the temperature at the critical grating/prism mount and keeps that temperature to within ±0.05 °C by switching on and off a heating tape which surrounds the spectrometer baseplate. The system largely eliminates intensity drifts due to wavelength and order changes as long as the other contributing factors which influence the heat gain/loss characteristics of the spectrometer (i.e., room temperature, exhaust system flow rate, solvent being aspirated, and alignment of the plasma plume) are reasonably well controlled.

Table 8 presents the results of a homogeneity study of SRM 2673 (Urine) in which calcium was determined directly using the 445.478 nm Ca line. Nine discreet samples at each of the two levels were analyzed after a dilution of 3:25. The determination was a test not only of the ability of the temperature regulation system to maintain stable spectrometer conditions, and thus allow a highly precise determination, but also of the reaction of the sample introduction system to a very complex matrix (high alkali and organic content). The use of a standard addition technique was required; an 85 percent recovery of spiked calcium was found. The analytical precision obtained (0.6 to 0.9 percent RSD) is limited by the sample transport system. Further refinements are being investigated to improve the precision of the method.

Table 8.

Urine Sample	Ca, µg/mL
Normal Trace Constituent Level	105.3 ± 0.9[a]
Elevated Trace Constituent Level	105.7 ± 0.6[a]

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[a] ± one standard deviation of the mean.

12. Determination of Ultratrace Concentrations of Chromium by Isotope Dilution Mass Spectrometry (14215)

K. A. Brletic, L. J. Powell

Because of its role as an essential trace metal, the accurate analysis of chromium has been of great concern to nutritionists over the past 10-15 years. The analysis of chromium has proven to be difficult due to the chemical complexity of the element and the fact that chromium is present at low or sub-nanogram per gram concentration levels in most biological samples. As a result, recent studies have indicated that many of the earlier literature values for chromium in biological materials are in error [1].

A previously developed isotope dilution mass spectrometric technique provided accurate analyses of chromium in a variety of environmental, botanical, and biological matrices [2]. However, this technique lacked sensitivity, making it difficult to analyze many of the critical biological samples such as serum and urine.

The chemical preparation involves spiking the sample with one microgram of ^{50}Cr, dissolution with nitric and sulfuric acids, and separation of chromium by solvent extraction into methyl isobutyl ketone. The chromium is back extracted into water and reduced with a HNO_3-H_2O_2 solution prior to analysis.

A new mass spectrometric procedure, which improves the instrumental sensitivity for chromium by more than a factor of fifty, has been developed. This method involves the sequential drying of silica gel, chromium(III) nitrate and boric acid onto a rhenium filament. The filament is then transferred to a nitrogen atmosphere and heated to 830 °C using an optical pyrometer to precisely control the filament temperature. This sample mounting procedure is the critical step in achieving ion currents of $3\text{-}5\times10^{-11}$A for 250 nanograms of chromium.

This method has been applied to SRM 1253, Phosphorized Copper and SRM 1577a, Bovine Liver, with excellent results. During the next year, plans are being developed to look at other matrices such as SRM 1549, Powdered Milk (in which the chromium concentration is estimated to be less than 50 nanograms per gram) and human body fluids which are thought to contain less than one nanogram per gram of chromium. The determination of chromium in body fluids will pose a particular challenge because the accuracy of the analysis is highly dependent on the magnitude and variability of the analytical blank. To analyze these materials, the blank must be controlled at the picogram level, a project which will require significant research to identify and eliminate sources of contamination, while maintaining sufficient chemical recovery of the chromium.

References

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13. Improved Radiochemical Procedures for High Sensitivity Measurements of Ultratrace Concentrations of Tin and Mercury (11310)

R. R. Greenberg

Although instrumental neutron activation analysis can be used to determine a large number of elements in most matrices, some critical elements are frequently obscured by high background levels of radiation or by interfering elements. With appropriate radiochemical separations, a large number of additional elements can be determined at the ppb and even sub-ppb levels. Tin and mercury are two elements which are of both environmental and biomedical importance. Although radiochemical separation procedures have been previously developed for these elements, recent applications have required better sensitivity and therefore improved separation from interfering elements.

Tin has previously been separated from Orchard Leaves (SRM 1571) with an iodide extraction into toluene. However, approximately one percent of the selenium was found to accompany tin through this procedure which elevated the background level of radiation. Although this did not seriously affect the determination of tin in Orchard Leaves or Citrus Leaves (SRM 1572), it did produce serious problems in other materials such as Bovine Liver (SRM 1577) and human livers from the National Environmental Specimen Bank (NESB) program. Several modifications in the procedure, including a selenium volatilization step after sample dissolution (using H_2O_2 and HF), a pre-extraction wash with chloroform, and a back-extraction of tin into an aqueous Na_2EDTA solution, reduced the fraction of selenium accompanying tin to ≤ 0.05 percent. With these modifications, the tin content of Bovine Liver (SRM 1577) was found to be 20 ± 3 ng/g (1s for six samples). The tin concentrations in eleven human livers were also determined. Four subsamples of human liver homogenate were analyzed and the precision was better than one percent (1s).

Mercury has previously been separated from a number of matrices by solvent extraction using nickel diethyldithiocarbamate $[Ni(DDC)_2]$ in chloroform. Large fractions (10-50 percent) of copper and bromine accompany mercury and can interfere with the ^{197}Hg isotope by elevating the background level of radiation. A small fraction of the selenium (≤ 0.01 percent) also accompanies mercury and directly interferes with the 279 keV γ-ray of ^{203}Hg. Two additional steps were found to greatly improve the separation of mercury from these other elements. The use of a chloroform wash prior to extraction with $Ni(DDC)_2$, and a post extraction wash with aqueous Na_2EDTA reduced the accompanying copper and bromine by a factor of 3-10, and the selenium by a factor of 10-100. With these modifications no selenium could be detected in any of the samples via other, more intense γ-rays. These improvements allowed mercury to be determined in Bovine Livers (SRM's 1577a and 1577b) at the 3-5 ng/g level with uncertainties of only 2-3 percent (1σ) due to counting statistics. SRM 1577 (Bovine Liver) was analyzed as a control and the present value of 16.0 ± 0.3 ng/g (1σ counting statistics) clearly demonstrates the improvement in the method when compared to the previously determined value of 16.8 ± 0.9 ng/g (1σ); the uncertainty due to counting statistics has been reduced by a factor of three.

In summary, the modifications described greatly improved the separation of tin and mercury from other, interfering radionuclides. As a result, the detection limits for both elements were greatly reduced, and the analytical uncertainties due to counting statistics were significantly reduced.

14. Isotopic Fractionation of Gallium on an Ion Exchange Column (11310)

J. W. Gramlich, L. A. Machlan

The possibility of isotopic fractionation during ion exchange purification has serious consequences for isotope dilution mass spectrometry and geochronological isotope ratio measurements. Unless quantitative isotopic recovery is achieved from the ion exchange separation, biased results may be generated. Isotopic fractionation during ion exchange separations has been reported in the literature for some elements such as calcium, potassium, and chlorine; however, these studies have received little attention and have been generally overlooked or disregarded by scientists engaged in ion exchange separations for isotopic analysis. The work reported here confirms that isotopic fractionation can occur during chemical purification and emphasizes the importance of careful examination of all possible sources of systematic bias during the development of a chemical separation and purification procedure.

Previous studies by the Mass Spectrometry Group have indicated isotopic variations in high purity gallium metal. For example, high precision measurements of the ^{69}Ga/^{71}Ga ratio on 15 samples from different lots and a number of worldwide, commercial manufacturers show a 0.25 percent variation in the isotopic ratio. The general trend of decreased ^{69}Ga/^{71}Ga ratio with increasing purity implies that isotopic fractionation takes place during the purification process. In order to ascertain whether the isotopic variations are natural or are due to the purification process, it is necessary to survey the gallium isotopic composition in natural ores.

Gallium is difficult to purify from natural materials because iron, which is difficult to separate from gallium, strongly interferes with the mass spectrometric measurement. In an attempt to quantitatively separate iron from gallium, an anion exchange column in the thiocyanate form was utilized. Yields from the column were extremely low (25-30 percent recovery) and the recovered gallium was depleted in ^{69}Ga relative to the expected value. Measurement of the gallium fraction that had remained on the column showed an enrichment in ^{69}Ga.

An experiment was conducted to quantitatively evaluate the rate of elution from the column and the isotopic composition in each eluted fraction. Two columns were set up and approximately 200 mg of gallium with a measured isotopic composition of ^{69}Ga/^{71}Ga = 1.5283 ± 0.0001 (1s) were loaded onto each column. Twelve elution fractions were collected from each column after which the columns were stripped to remove any remaining gallium. A weighed portion of each of the fractions was spiked with ^{71}Ga for isotope dilution analysis to determine the gallium content while the remainder of the fraction was used to determine the isotopic composition. Both column experiments confirmed the initial observation of column fractionation. Ratios ranged from ^{69}Ga/^{71}Ga = 1.5148 for early fractions off the column to 1.5308 for the final stripping fraction.

15. Improved Sensitivity in Instrumental Activation Analysis Using the Compton Suppression Technique (14301)

J. R. Vogt, R. L. Zeisler

A persistent problem in instrumental activation analysis is the reduction of sensitivity caused by background events in the gamma-ray spectra resulting from Compton scattering within the detector. While this problem is less severe with large germanium detectors than with sodium iodide detectors--primarily because the higher resolution and higher atomic number of germanium increases the peak-to-Compton ratio--the Compton background still precludes reaching the ultimate sensitivity of the detector. The usual technique that has been used to reduce the background from Compton events is to surround the primary detector with a second detector--usually sodium iodide--in an anti-coincidence mode. Detection of Compton scattered photons in the secondary detector blocks pulse conversion in the analog-to-digital converter.

Although many Compton suppression systems have been described in the literature during the past twenty years, only those associated with low level counting of environmental radioactivity or with prompt-gamma activation facilities appear to be used routinely to produce quantitative data.

During the past year, a Compton suppression system has been set-up and evaluated. The system consists of a NaI(Tl) annulus and an integral line NaI(Tl) well detector used to surround all but the rear of the 19 percent, 1.79 KeV Ge(Li) primary detector. The electronics consist of an anti-Compton analyzer (containing the coincidence circuitry) and an amplifier. A random pulse generator is used to correct the gamma-ray photopeak areas for losses due to the coincidence system and pulse pile-up. For this system, the sample is inside the NaI(Tl) anti-Compton shield, rather than outside as in some other designs. Since there is no detection of scattered photons in the forward direction [to the rear of the Ge(Li) detector], the suppression at lower spectral energies is not as good as in systems where the Ge(Li) detector is surrounded more completely. However, the suppression factor on the Compton edge for Cs-137 is still about eight, for the middle of the spectrum about 4-5, and at the back-scatter peak about 3.5. Since the improvement in sensitivity follows roughly the square root of the background, the increases in sensitivity for these portions of the spectrum are approximately 2.8, 2.1, and 1.9, respectively.

With the sample inside the NaI(Tl) shield, both coincident photopeaks and Compton events for radionuclides with cascading transitions are suppressed. This effect reduces the spectral background more than simple Compton suppression. There are both positive and negative effects of the suppression of coincident gamma-rays. The positive aspect is that the sensitivities of non-coincident gamma-rays are improved. This can be of benefit in matrices where coincident gamma-rays account for a substantial part of the activity, such as Sc-46 in environmental materials and Na-24 and Br-82 in biological materials. For example, in SRM 1633a, Fly Ash, the values obtained using Zn-65 are 238.0 ± 6.6 ppm (2s) without the Compton suppression system, and 227.1 ± 2.2 ppm (2s) with the Compton suppression system. The certified value is 220 ± 10 ppm. The negative aspect is that the sensitivity and accuracy of radionuclides having coincident gamma-rays are reduced. This is particularly significant for longer lived radionuclides for which coincident gamma-rays are common.

The loss of photopeak counts due to coincidence losses and pile-up can be corrected to less than ±1 percent using a random pulser, up to a non-suppressed ADC deadtime of 10 percent. At higher deadtimes--such as may be necessary to obtain significant counting rates for low levels of short half-life radionuclides--the system tends to become erratic and is not readily correctable. This tends to explain why--as noted earlier--quantitative data in the literature using Compton suppression are associated with applications involving low level counting and prompt-gamma activation, where the deadtime is usually <10 percent.

Overall, the system does improve the sensitivity of activation analysis for radionuclides which do not have coincident gamma-rays or relatively short half-lives. This sytem should be particularly appropriate for chromium, and investigations involving this element are in progress.

16. Development of an Isotope Dilution Mass Spectrometric Procedure for Iodine in Botanical Materials (11310)

J. W. Gramlich, T. J. Murphy

Iodine is an essential trace element, yet it's concentration is not certified in any of the food or botanical type Standard Reference Materials (SRM's). While some of these SRM's have "information" values for iodine (provided by neutron activation analysis), they could not be certified since they were determined by only one technique. Therefore, a research program was initiated to develop an isotope dilution mass spectrometric method for trace iodine in botanical materials.

Since iodine is a mononuclidic element, a radioactive isotope was selected for spiking. SRM 4949, Iodine-129 Radioactivity Standard, was selected since ^{129}I has a half-life of 1.6×10^7 years and the SRM has a favorable $^{127}I/^{129}I$ ratio of 0.16. It was necessary to stoichiometrically equilibrate the spike isotope and the natural iodine of the sample. Various wet-ashing methods were studied using ^{125}I as a tracer. The method developed was shown to quantitatively retain iodine by oxidation to iodate while destroying the botanical matrix.

In brief, the procedure involves transferring a sample of the botanical material to a FEP-Teflon bottle and spiking with a known quantity of ^{129}I. The spiked sample is wet-ashed with fuming nitric and perchloric acids. The solution is then diluted, transferred to a centrifuge tube, and the insoluble potassium perchlorate separated. Iodate is reduced with a hydrazine solution and the resulting iodide is coprecipitated with chloride by the addition of silver nitrate solution. The mixed AgCl-AgI precipitate is separated by centrifugation, washed with dilute ammonium hydroxide solution to remove most of the AgCl and dissolved in ammoniacal cyanide solution for mass spectrometric analysis.

Ionization and mass spectrometric analysis of iodine as a negative ion requires an ionization filament with a very low work function to produce a favorable ratio of charged to neutral species. Filament materials normally used for positive ion mass spectrometry do not meet this requirement; however, LaB_6 has a very low work function (approximately 2.6 eV). The procedure developed for the iodine mass spectrometry involves the coating of a rhenium filament with lanthanum hexaboride by electrophoretic deposition from an anhydrous methanol suspension of the compound. The filament is then heated in a vacuum to sinter the LaB_6 and to remove surface adsorbed impurities which poison the filaments; adsorbed gases form a dipole layer at the surface of the filament which modifies the surface potential and work function. The iodine as AgI is then loaded onto two side sample filaments of a triple filament ion source. The use of LaB_6 as the ionizing filament has improved the sensitivity for iodine measurement by approximately 10^4 over techniques previously used in this laboratory. Intense and sustained ion beams can be produced on samples containing as little as 10 nanograms of iodine.

This new method has been applied to the determination of iodine in SRM 1577, Citrus Leaves. The value found, 1.88 ± 0.12 (2σ) $\mu g/g$, is in excellent agreement with the neutron activation value of 1.84 ± 0.14 (1σ) μg/g. On the basis of these determinations, the concentration of iodine in this SRM will be certified. This will be the first botanical SRM to be certified for trace iodine concentration. The method will be applied to other SRM's in the near future.

17. Ion Optics of Magnetic Sector Mass Spectrometers (11310)

I. L. Barnes, W. A. Bowman, P. A. Morales

A program has been initiated to establish the theoretical background for the design and construction of new mass spectrometers using other than normal field entry, referred to as "off axis entry" mass spectrometers. The critical parts of this program have been limited to magnetic sector instruments, with the addition of multi-component systems such as electrostatic sectors, quadrupoles, hexapoles, and solenoids to come later. It was also decided at the beginning of the program that only "real" systems would be considered even though it was realized that this would greatly complicate the program. This meant that magnetic stray fields would be considered, and that only ion beams of finite height and width would be used. Thus, the first two areas studied were stray fields and the mathematical formulation of the passage of ion beams through magnetic sectors.

Historically, stray fields have been considered in the design of mass spectrometers using an approximation based on a simple function of the magnetic gap, though it has long been recognized that this was, at best, a crude approximation. To better understand the magnitude and shape of the stray field, two gaussmeters were carefully calibrated. One was used to control the field while the other, mounted on a precision slide was used to measure the field at 5 mm increments from within the magnet to 40 cm away. Measurements were made on a line normal to the pole face, at various angles inclined to the face, on a line 0.5 cm up from the center and on each side of the center line; thus, a map of the field was obtained.

With the help of K. Eberhardt of the Statistical Engineering Division, it was determined that the data were best fitted by a hyperbolic expression of the following form:

$$y = \frac{K}{1 + \exp\,(Bx+E) + \sqrt{\dfrac{(Bx+E)^2 - 4C(Ax^2+Dx+1)}{2C}}}$$

where y = field; x = distance; and K, B, E, C, A, and D = constants. A plot of this function is shown in Figure 21 (solid line). The measured points are shown as open circles. The above expression is valid for all fields from 1000-9000 gauss and examination of the residual errors indicates that each point is fitted to within 1 percent. The above measurements indicate that within the experimental error, the NBS 90° magnet produces a uniform field every place within 2 cm of an edge. Data obtained in a repeat of the experiment, at the University of Mexico with a magnet of different design and gap width, fit the same expression with only slight differences in the constants. Although a universal formula has not been found, its development does appear

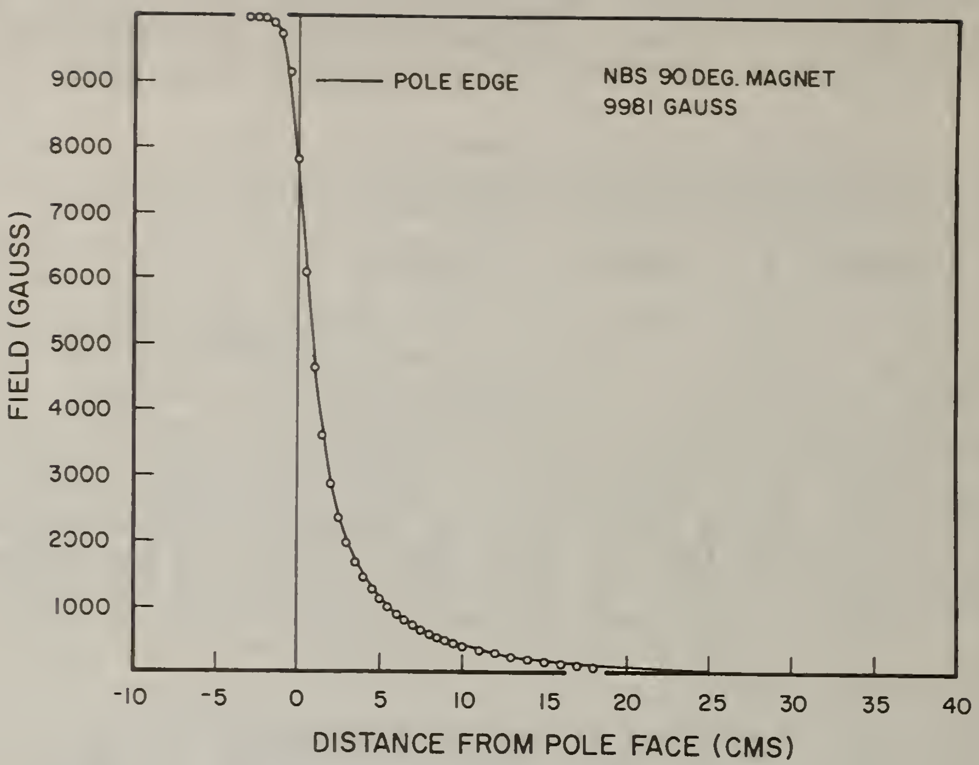

Figure 21. Plot of measured field versus distance from magnet pole face. Measured values (o); calculated values (——).

to be possible. While the above expression cannot be directly integrated, numerical methods such as cubic splines and Simpson's method have been used with sufficient accuracy. A repeat of the experiment inside of a flight tube gives identical results indicating that the normal construction materials have no effect on the stray field.

In conjunction with studies of stray fields, a general investigation of ion optics has been conducted and has provided significant improvements in the design of the NBS mass spectrometers. A charged particle leaving a source at a small angle to the normal and with a small change in energy yields a set of five equations of motion with 27 terms each and 8 unknowns. To solve these, at least three parameters of the instrument must be fixed. The resulting equations are then best solved using a matrix transformation method. This has been done utilizing the NBS Univac 1100/82 and a matrix program called "TRANSPORT" originally written at the Stanford Linear Accelerator Laboratory. This has been very useful but unfortunately gives the position of the ions only at the beginning and end of the flight path. To further explore the effects of the field, "TRANSPORT" was used to rapidly choose a promising geometry and this information was used in a program called "MASMEX" that was written at NBS to trace up to 27 different ions through that geometry, with the position of the ions given in 1 mm increments. Currently, a graphics program to plot the enormous amount of data obtained from this program is under development.

As a result of the work done during the past year, it has been determined that the best focussing properties for a particular geometry are strongly related to the ratio r = gap height/radius. However, this ratio is limited to a range of 0.05 to 0.144. In addition, the off-axis angle of entry of ions for best focussing of ions is a function of this ratio and varies from 24° to 32°. Thus, the gain in dispersion that may be obtained varies from 1.8 to 2.6. There are several new configurations that need to be carefully examined since in these cases, the stray field seems to have an important influence on the dispersion gains. Further work in this area is necessary but new mass spectrometer designs with greatly increased capabilities seem assured.

18. The Use of a Chromium Internal Standard for the Analysis of Diverse Iron-Chromium-Nickel Alloys (14301)

D. E. Brown, J. A. Norris

Emission spectrochemical analyses normally require standards which closely match the matrices of the unknown samples and which cover the concentration ranges of the elements present in the unknowns. In the homogeneity testing and analysis of candidate Standard Reference Materials (SRM's) covering a wide range of matrices and elemental concentrations, it is not always possible to have standards that totally match the unknown.

One approach to the analysis of a wide variety of iron-chromium-nickel alloys is the use of a chromium internal standard. In Table 9, a representative selection of Fe-Cr-Ni alloys and their matrix compositions are shown. In addition to the elements given in the table, many of these alloys contain significant amounts of W, Ti, Al, V, Nb, and Ta. At the present time, over 40 separate alloys are available as SRM's. Chromium is not presently being used as an internal standard in tertiary alloys; however, it is the best candidate for use as an internal standard. The nickel concentration in these alloys is more variable while the iron concentration is typically determined by difference. In addition, the use of iron as an internal standard would require a complete sample analysis since the concentration ratio method of curve plotting is necessary as a result of the considerable matrix variations.

Table 9. Fe-Cr-Ni Alloys.
Values in %

Alloy	Fe	Cr	Ni	Co	Mo
Stainless Steel	60-80	13-24	7-24		
Incoloy	36	13	40		6
Inconel	10	16	74		
Hastelloy	23	21	46		9
Waspaloy	2	19	56	13	
Rene-41	0.5	20	53	12	10

Since chromium is independently determined, the sample analysis need not be complete and the ratio of the desired element to chromium concentration is all that is required for instrument calibration. High concentrations of elements such as Co, Mo, and W can cause direct element line interference problems on the available vacuum spectrometer. When this occurs, the particular standard involved is not used for the element or elements in question.

Using this technique, it has been possible to calibrate the vacuum spectrometer for the elements C, P, S. Mn, Si, Ni, Fe, V, Ti, Mo, Cu, Co, Sn, Al, Nb, Ta, Zr, B, Pb, and W. With these instrumental curves, routine homogeneity tests have been run on new SRM's 1244, 1245, 1246, 1247, C2400, C2400a, C2401, C2401a, and C2402, while simultaneously providing approximate analyses for future quantitative chemical determinations. Typical results for the C2400-C2402 series SRM's are given in Table 10.

Table 10. Homogeneity Test Values.

	Carbon		Phosphorus		Sulfur	
SRM	Level	%RSD	Level	%RSD	Level	%RSD
2400	.043	4.38	.016	2.64	.001	18.5
2400a	.039	4.17	.012	4.06	.002	14.7
2401	.066	3.79	.025	2.56	.030	2.28
2401a	.037	9.55	.013	5.08	.015	4.75
2402	<.02		.017	4.25	.027	3.50
	Manganese		Silicon		Nickel	
2400	.74	1.55	.61	2.49	3.43	2.38
2400a	.60	1.44	.62	2.52	3.12	1.67
2401	1.10	1.51	.80	2.34	3.87	2.80
2401a	.83	1.21	.76	1.89	3.55	2.35
2402	.70	3.29	.91	4.04	50.5	1.00
	Iron		Vanadium		Molybdenum	
2400	73.8	.17	.09	2.79	.25	2.35
2400a	74.5	.16	.04	2.56	.10	2.32
2401	63.3	.19	.22	2.53	2.22	1.87
2401a	63.5	.17	.15	1.68	2.13	1.66
2402	8.7	2.87	.29	4.36	13.7	2.82

19. Development of a Precise Static Leach Test and the Evaluation of Simulated Nuclear Waste Glasses for a Reference Material (11310)

M. S. Epstein, H. M. Kingston, W. F. Koch, G. Marinenko,
D. J. Cronin (Div. 565)

One long range goal of nuclear waste storage is the development and promulgation of a precise and accurate nuclear waste leaching test. Studies at NBS have produced a significant breakthrough in the ability to obtain reproducible leach results. Previously, the results of similar tests were found to differ by as much as an order of magnitude for replicate samples. Recently, a round robin study was conducted by 25 national and world laboratories; the results of the study showed poor agreement among these laboratories in a specific static leach test coordinated by the Materials Characterization Center (MCC) of the Department of Energy.

The existing static leach test MCC-1 was used as the starting procedure for the work carried out at NBS. The variables in the test were identified both theoretically and through data provided by the MCC. As a result, the test was redesigned in specific areas to eliminate many variables by providing more stringent control of temperature, surface roughness, Eh, CO_2 (pH interferent), and leachant loss during the test. In order to carefully control these parameters, a distilled water leaching system was designed which maintained, monitored, and recorded the above conditions for 28 days.

In addition to controlling the test parameters, the potential of a reference simulated nuclear waste glass was evaluated. One complex base glass reference material and 12 additional glasses having modified compositions were made at NBS. Each of the 12 modified glasses were a statistically engineered compositional variation of the base glass. The analytical results from these 12 altered glass matrices provided valuable information about the separate components of the glass system. A 13-component empirical equation was designed to statistically evaluate the influence of each component on the leach characteristics.

Statistical evaluation of the leachate data for 12 pairs of glasses and of the seven replicates of the base glass showed a high degree of precision in the 28 day modified leach test. The precision does not resemble the poor reproducibility normally obtained from current leach data but is more similar to the reproducibility expected of compositional analysis. For seven of the nine elements tested, no significant error component larger than the error associated with the dc plasma elemental measurements of the leach solutions could be identified. The uncertainty at the 1s level of the seven base glass replicates is within the measurement uncertainty of the instrumental techniques used to analyze the final leachate solutions.

On the basis of these results, the Materials Characterization Center has designated the base composition of simulated nuclear waste glass to be the future reference material. It will be made in a large quantity and distributed as a reference for all future leaching work related to nuclear waste materials and mechanisms.

In addition, information on the significance of glass homogeneity was obtained, the simultaneous elemental determination of a selected group of elements was accomplished, and certain mechanistic information was obtained that explained why the uncertainty for Zn was approximately 10-20 percent. The major source of this uncertainty was non-reproducible adsorption onto the container walls during the 28 day test.

It is anticipated that after the production of the reference glass, this specialized equipment will be used to elucidate subtle mechanistic information which will further refine this relatively new field of analytical measurement.

20. New Concepts in the Design and Fabrication of Fluorescent Glass Standards for Use in Nondestructive Crack Testing (11310)

R. W. Burke, D. K. Hancock

Fluorescent dye penetrant testing continues to be one of the most widely used nondestructive methods for detecting minute cracks and flaws in metallic surfaces. The basic test, as currently performed, is essentially the same as originally developed. It entails coating the part to be tested with the fluorescent dye penetrant, wiping off the excess dye from the exposed surface, applying a developer, and measuring the fluorescence of the resulting indication. While many improvements have been made in the formulation of highly sensitive penetrants, efforts to quantify reproducibly these improvements in terms of their relative fluorescent brightness and crack-measuring capabilities continue to be thwarted by the nonavailability of suitable fluorescent standards for calibrating the test equipment.

Initial efforts to develop fluorescent glass standards for use with various NDE tests led to a serious consideration of two types of standards. One consisted of a rectangular piece of uranium-doped glass mounted in a metallic heat sink for enhancing temperature stability; the other type was an assemblage of glass fibers having a series of graded diameters and uranium concentrations. The first type of standard was intended for the reproducible calibration of spectrofluorimetric instrumentation while the second type was envisioned as a working standard for improving the reliability with which the intensities and widths of fluorescent indications could be measured.

As a result of understanding more clearly the needs of industry and the problems associated with their "mass production," several changes in the makeup and design of these standards were considered desirable. During the past year, efforts have focussed on perfecting these changes. The most significant change was the decision to use an alternative fluorescent glass that could be substituted for the uranium-doped glass. Two factors were instrumental in this decision. The predominant factor was that the fluorescent temperature coefficient of uranium-doped glass is much larger than originally anticipated. Our measurements have shown that the fluorescence of this glass decreases approximately 0.9 percent per degree Celsius in the temperature range of 20-40 °C. A second factor was a safety issue involved in the in-house production and fabrication of uranium-containing materials. Subsequent studies showed that the fluorescence of terbium-doped glass is very similar to that of uranium-doped glass. Like uranium, terbium-doped glass fluoresces in the green region of the spectrum and as a consequence exhibits excellent coincidence with both the fluorescence of most dye penetrants and the mesopic eye response function. In addition, the range of fluorescent intensities obtainable with terbium-doped glass is relatively large since doping levels up to 45 to 50 weight percent are possible. Its main advantage for use as a standard, however, is the fact that its fluorescent temperature coefficient is at least an order of magnitude smaller than uranium-doped glass.

The other major change in the research effort has concerned the approach to producing a fluorescent standard that can be used in conjunction with the measurement of crack indications. Because of significant handling and mounting problems, the glass fiber approach has been replaced by a system in which fluorescent indications of varying widths and relative intensities are obtained by ruling a series of narrow slits in opaque films that have been evaporated directly on polished glass flats having different terbium concentrations. Six to eight slits per side are planned with widths ranging from 5 to 100 micrometers.

Current efforts are concerned with the systematic evaluation of the various formulations of terbium-doped silicate and phosphate glasses now on hand and the subsequent selection of one of these as the base formulation that will be used for the preparation of the two types of fluorescent standards being proposed. At the present time, the phosphate glasses have the apparent advantage because they are intrinsically more fluorescent. This property may be due to the fact that the phosphate matrix is more transparent to ultraviolet radiation and hence the energy reaching the terbium fluorophor is more intense. Once the optimum base glass composition has been chosen, it will be fabricated into forms that are easily incorporated into NDE tests. As an instrumental calibrant, particular emphasis will be placed on providing a configuration and size that is compatible with "typical" or most widely used commercial instrumentation. At the same time, the final decision will be made on which evaporated film will be used in the production of the simulated crack indication standard. The goal here is to identify a film that is durable, exhibits a matte finish which closely approximates that of a typical metal specimen, and can be properly ruled. Based on the projected progress, it is believed that samples of both types of standards will be ready for field evaluation in the near future.

21. Characterization of Selected Trace Elements in the Chesapeake Bay (11310)

E. S. Beary, J. D. Fassett, R. R. Greenberg, B. R. Hardas, W. R. Kelly, H. M. Kingston, J. R. Moody, T. C. Rains, W. S. Liggett (Div. 714)

Trace element measurements for a large multi-disciplinary study of the Chesapeake Bay have been completed. As part of this study, water samples were collected at 51 sites and both the particulate and dissolved fractions were analyzed for Cd, Ce (particulate only), Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sc, Sn, Th, U, and Zn. Two types of samples, surface and bottom, were collected and analyzed using specific chemical preconcentration and separation techniques developed for neutron activation analysis (NAA) and graphite furnace atomic absorption spectrometry (GFAAS). The data are the first environmental analyses of this kind to yield a data set at the 95 percent confidence limit that allows rigorous statistical evaluation of elemental relationships.

The concentrations of 14 elements in the dissolved fractions were evaluated by direct comparison with naturally occuring seawater levels. At several locations in the Bay, two toxic elements (lead and tin) were elevated by two orders of magnitude over normal seawater levels. Similar levels of organo-tin were found by other researchers. Most of the dissolved iron concentrations were approximately the same as that found in seawater. However, a number of bottom samples collected at some of the deepest locations had significantly greater iron concentrations. The elevated levels appear to be due to anoxic conditions in the bottom sediments. Similarly, the manganese concentrations had maxima at these same locations. Uranium and molybdenum were found in higher concentrations in seawater than fresh water. As a result, the concentrations of these two elements can be used to trace the seawater content of the water column throughout the Bay. The uranium isotopic ratios of seven selected samples were investigated and found to be normal to within 0.7 percent error. The dissolved thorium concentrations in samples taken near the mouth of the Bay were approximately two orders of magnitude greater than previously reported seawater values. The dissolved concentrations of the remaining elements (Cd, Cr, Co, Cu, Ni, Se, and Zn) appeared to be relatively similar to the levels normally found in seawater.

The information obtained from the raw particulate elemental concentration data has been difficult to interpret in the past. Since the concentrations were reported in elemental mass (ng) per unit volume (mL) of water, the total amount of particulate mass suspended at the time of sample collection strongly affected the results. Variations in current, tide, temperature, biota, wind conditions, etc. can greatly influence the total amount of particulate material suspended in the water column. To circumvent the problem of variable mass loading, a double normalization procedure was used to compute crustal enrichment factors. The concentration of each element in the sample was divided by the concentration of a reference element, in this case scandium, and the resulting value was divided by the ratio of these elements in average crustal material.

Scandium was chosen as a reference element because it has essentially no anthropogenic uses and its chemistry is relatively simple (single oxidation state, limited dissolved particulate interactions). The usefulness of this technique can be illustrated by comparing the variability in the cerium concentrations and the cerium enrichment factors (EF). The concentrations varied by a factor of 300 from site to site, while the EF varied by a factor of 1.5 and the observed standard deviation over the entire Bay was just 10 percent. The EF's for thorium were similar to those of cerium. Figure 22 was constructed to show all of these cerium EF's simultaneously. The environmentally active and anthropogenically abundant elements had significanly more complex ranges and patterns of enrichment factors than the elements used as multiple controls.

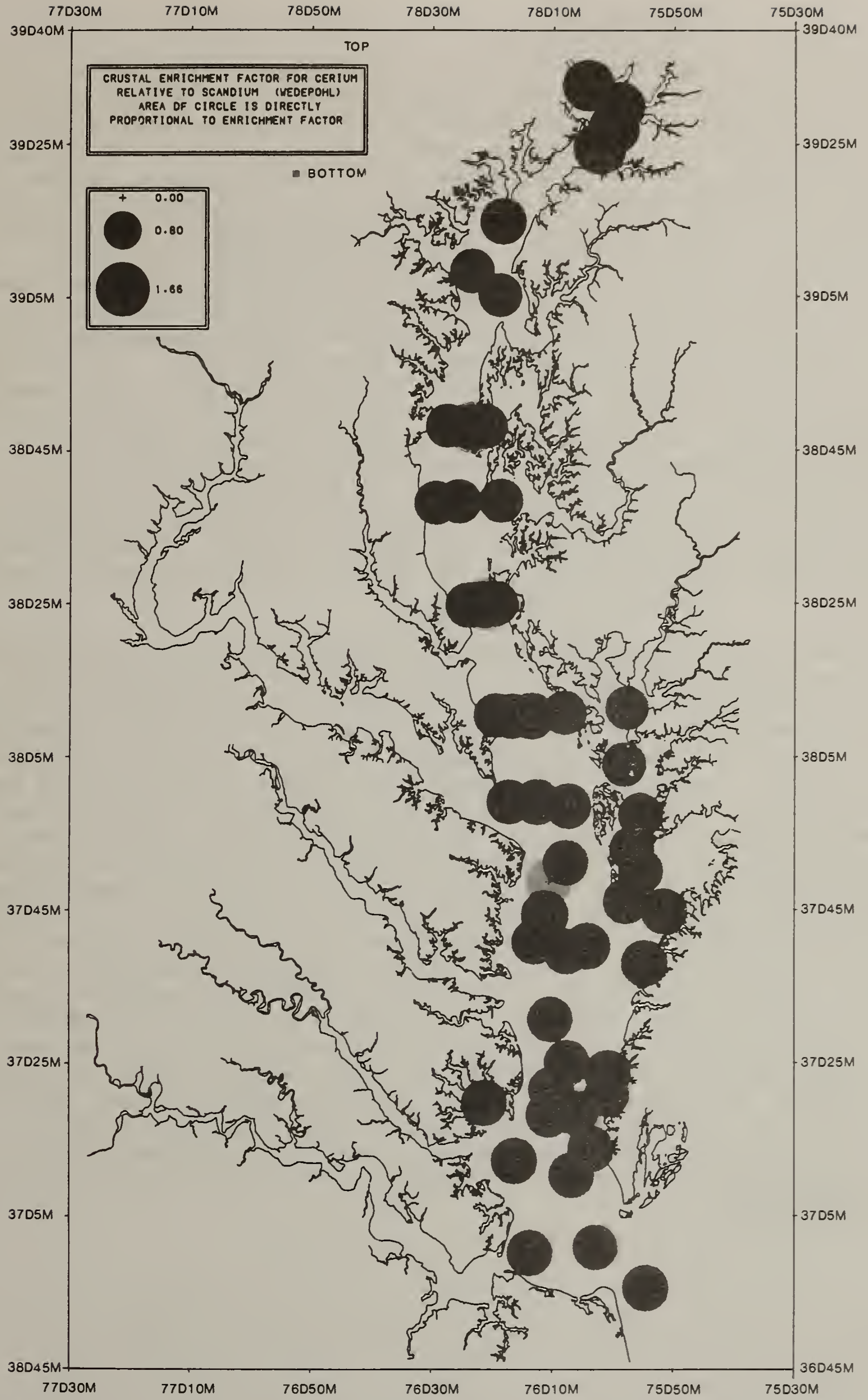

Figure 22. The crustal enrichment factors for cerium relative to scandium in the particulate fraction.

Almost all of the iron EF's were relatively similar to those of Ce and Th. However, a few samples had slightly elevated EF's. These samples were collected at some of the deepest locations within the Bay and appear to be linked to anoxic reactions in the sediment at these locations. The enrichment factors for cobalt, manganese, and nickel appeared to trace the flow of Potomac River water for quite some distance down the Bay. This was observed through the elevated EF's for the surface samples as compared to generally uniform EF's for the bottom samples. Figure 23 shows this relationship for cobalt. It was also found that a number of samples had greatly elevated cadmium enrichment factors. This appeared to be a result of crustal weathering of naturally occurring cadmium deposits and not anthropogenic sources. These deposits and their erosion have also been documented by other researchers. The enrichment factors for lead exhibited a great deal of variability; most of the samples had lead EF's approximately five (i.e., five times greater than Pb/Sc ratio for average crustal material). For the elements chromium, copper, and uranium, the enrichment factors appeared relatively similar to naturally occurring material. Molybdenum was below the detectable limits in most samples and tin could not be detected in any of the particulate samples. Zinc suffered from severe blank problems arising from the filter material used; however, samples near the top of the Bay had very high mass loadings and zinc appeared to be slightly enriched.

Although most elements were found at levels that could be explained by natural mechanisms, both dissolved and particulate lead and dissolved tin appeared elevated over normal at some locations. Using enrichment factors, the cobalt, manganese, and nickel clearly traced the flow of the Potomac River; however, it is not clear if the elevated EF's are due to natural or anthropogenic causes. The nature of the samples challenged several existing areas of analytical work. The analysis of ppb and ppt elemental concentrations in a salt matrix led to a new separation preconcentration method for neutron activation analysis. This procedure provides solid resin pellets containing 16 trace elements with no alkali, alkaline earth, or halogen element interferences. These pellets are placed directly into the reactor for irradiation. In addition, the statistical evolution of extensive blank data helped to characterize blank behavior at these ultra-trace levels and showed the inadequacies of using a normal distribution. Lastly, the 2-3 orders of magnitude fluctuation of the particulate concentration data led to the application of enrichment factors which have been used in air particulate analyses but had not been applied to a aqueous systems. The choice of a reference element and secondary check elements also proved ideal. This technique provided a means by which the data and its environmental significance could be evaluated based on statistical concepts. Additional work is currently in progress with the Statistical Engineering Division to investigate additional correlations within these data sets.

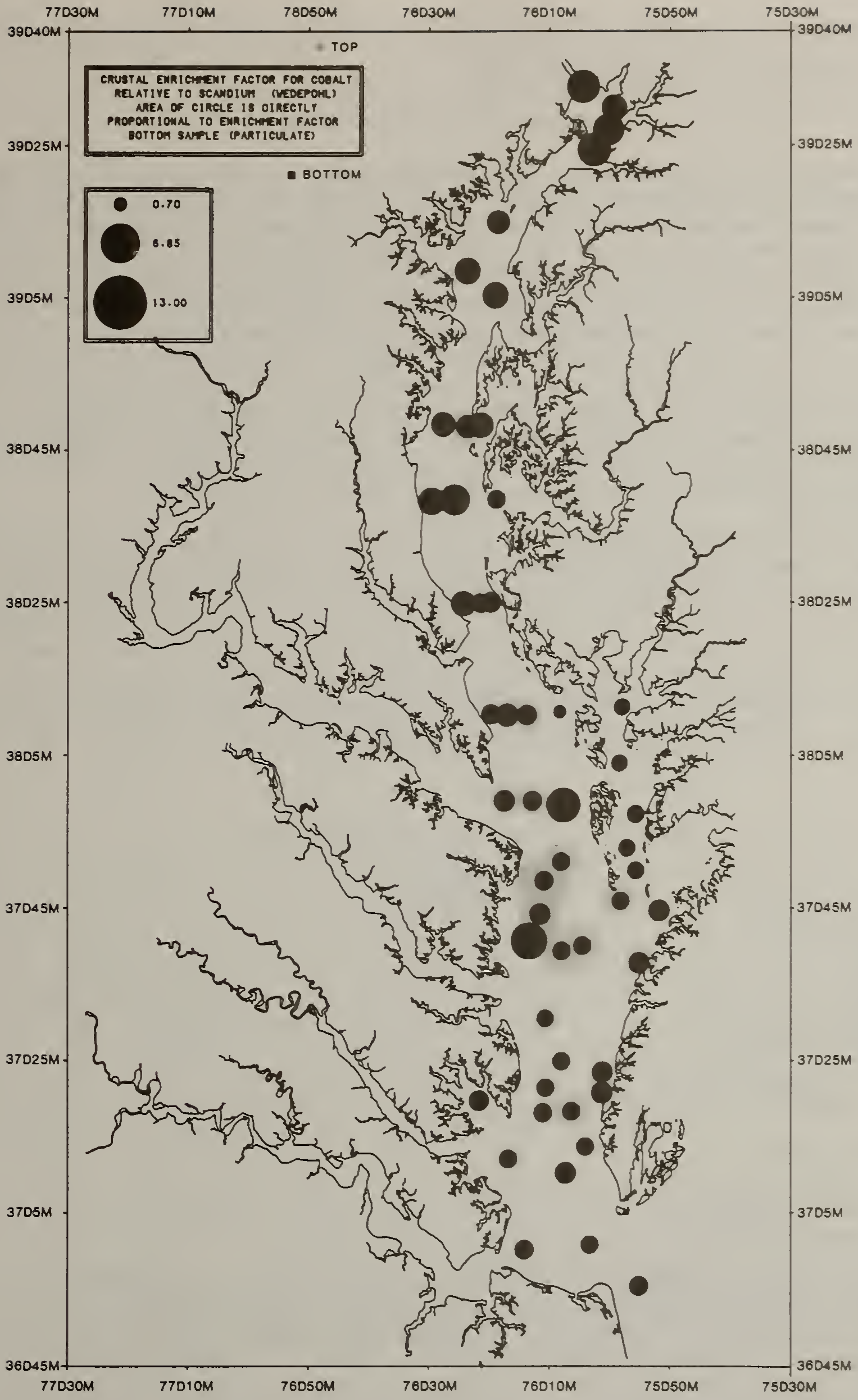

Figure 23. The crustal enrichment factors for cobalt relative to scandium in the particulate fraction.

22. Research to Develop Isotope Dilution Mass Spectrometry for Ultratrace Concentrations of Cadmium (14301)

J. D. Fassett, W. R. Kelly, E. A. I. Michiels

The certification of materials for low-level or ultratrace (sub ng/g) constituents has become increasingly important to satisfy both present and future needs for quality assurance in critical segments of industry, public health, and environmental monitoring. The use of microchemistry combined with pulse counting mass spectrometry results in the requisite sensitivity for the determination of ultratrace components from complex materials. Under clean room conditions, it is possible to separate an element from grams or less of starting material and determine isotopic composition and elemental concentration with a high degree of accuracy. Because of the biotoxicity of Cd, the ability to measure its concentration at low levels in subgram samples with high precision and accuracy is essential for establishing natural levels and detecting anthropogenic contamination. A procedure has been developed to determine cadmium at ultratrace levels in biological materials.

The fundamental limitation on accuracy and precision in ultratrace measurement is the magnitude and uncertainty in the chemical blank, where the chemical blank arises from dissolution and separation of the samples and mass spectrometric loading. As a result, the research required to create a successful analytical procedure for ultratrace measurement necessitates extensive effort to develop clean and efficient chemical dissolution and separation procedures, as well as extensive effort to identify and to quantify all sources of blank. The primary sources of blank were studied and are summarized in Table 11.

Table 11. Sources of Cadmium Blank.

	Determinations	Range
Reagent blanks		
HNO_3	3	0.6-5.3 pg/g
HCl	3	1.5-5.7 pg/g
$HClO_4$	2	27,30 pg/g
HBr(ACS)	1	650 pg/g
HBr(cleaned)	1	10 pg/g
Column Blank (1.5 mL resin)	1	62 pg
Loading Blank	5	2.2-2.9 pg
Total System Blanks	5	65-190 pg

The yields of several alternative chemical separation procedures were verified through radioactive tracer experiments both on synthetic samples and real blood samples. A comparison of procedures using strongly basic anion resin in the bromide and chloride forms was made. The higher blank of the bromide system discounted the increased efficiency of separation achieved. Thus, the selected procedure used two anion exchange columns in the chloride form: a 1 mL column for the separation of Cd from all other elements and a second very small (0.06 mL) "clean-up" column.

Samples of blood weighing about two grams were spiked with ^{111}Cd and dissolved using wet ashing oxidation. The Cd was separated and mass spectrometrically analyzed using a single filament silica gel technique which entailed drying sequentially layers of silica gel, sample, and phosphoric acid on the surface of a rhenium filament. The sample loading procedure was critical in achieving good signal intensity. The analysis was done at 1100 °C. Both ^{114}Cd/^{111}Cd and ^{112}Cd/^{111}Cd ratios were measured which allowed internal normalization corrections for isotopic fractionation to be made.

Four CDC bovine blood samples were analyzed. The cadmium concentration of these samples ranged from 7.01-7.09 ng/g. The internal normalization procedure improved measurement precision by a factor of three (1.6 to 0.50 percent, 1σ) as well as resulted in a +5.0 percent correction due to isotopic fractionation. Blank corrections were typically 0.5 percent. Although these bovine blood Cd concentrations were much higher than expected, the procedure developed here would allow analysis of the blood from "normal" humans containing cadmium levels of 0.3-0.6 ng/g with predicted uncertainties better than 10 percent.

23. The Use of Round Robins to Evaluate State-of-the-Art Uranium and Plutonium Measurements by Thermal Ionization Mass Spectrometry (11310)

J. D. Fassett, J. W. Gramlich, W. R. Kelly, L. A. Machlan

One of the best ways of standardizing and improving both measurement practices and techniques is by interlaboratory analysis programs or round robins. When properly designed and managed, round robins can be used to define and advance the state-of-the-art of a technique. Work was completed during the last year for two round robin programs designed to investigate different aspects of the measurement of uranium and plutonium. These programs are traceable to a national measurement base since all measurements can be directly related to well-characterized assay and isotopic Standard Reference Materials. To the international nuclear scientific community which participated in these round robins, the quality and uniformity of measurement of the safeguarded, fissionable isotopes of uranium and plutonium have profound implications for standardization and new methods research.

Initially, NBS participated in the interlaboratory experiment IDA-80 (Isotope Dilution Analysis, 1980) which was managed by the Safeguards Project of the Federal Republic of Germany in cooperation with more than 50 other laboratories worldwide. The program was designed to assess the precision and accuracy of U and Pu elemental concentration measurements and isotopic compositions in solutions from nuclear installations and reprocessing plants. IDA-80 was based upon a similar round robin program, IDA-72, which had 22 participants and was completed in 1975.

NBS and the Central Bureau for Nuclear Measurements (CBNM), Geel Establishment, Belgium, jointly provided assay and isotopic reference values for the uranium and plutonium samples used in IDA-80. IDA-80 differed from IDA-72 in that for IDA-80 an evaluation of accuracy was possible, since all reference measurements were traceable to NBS Standard Reference Materials. Thirty-nine samples were analyzed at NBS including: input from a reprocessing plant, both spiked and unspiked samples; synthetic uranium and plutonium mixture(s), both spiked and unspiked samples; and a mixed uranium and plutonium spike. At NBS, the unspiked samples were spiked with aliquots of SRM 933 (^{235}U) and SRM 996 (^{244}Pu) and separate aliquots of the samples were spiked with the spike solutions provided. All samples were equilibrated using an oxidation-reduction procedure. The uranium and plutonium were then separated and purified by anion exchange chromatography.

Plutonium samples were analyzed by high sensitivity thermal ionization mass spectrometry using ion counting detection. A one nanogram sample was required for each measurement. Uranium was analyzed by thermal ionization mass spectrometry using Faraday cup detection and triple filament loading of a 4 μg sample for each measurement. Isotopic fractionation corrections were made relative to SRM 947 where the $^{240}Pu/^{239}Pu$ ratio was measured to 0.06 percent (1σ, N=28) and SRM U-500 where the $^{235}U/^{238}U$ ratio was measured to better than .02 percent. Measurement precisions were better than 0.1 percent for all samples with excellent agreement between NBS and CBNM measurements. This level of agreement between the laboratories providing baseline values now make it possible to complete the most extensive and meaningful evaluation, national as well as international, of laboratories conducting safeguards measurements.

A second round robin investigating the high sensitivity measurement of uranium and plutonium loaded onto anion exchange resin beads was conducted by NBS and completed in the past year. The resin bead technique has been proposed for use in routine analysis of nuclear materials especially suited for reactor dissolver solutions formed in fuel reprocessing. This technique is innovative in both the sampling step and the use of high sensitivity pulse counting detection for isotopic ratio measurements. The resin bead provides the matrix for separation, physical transportation, and thermal ionization. High sensitivity detection is necessitated by the nanogram size samples which are used to minimize radioactivity. Eight laboratories participated in the round robin, five of which reported results for all samples. The size of the round robin reflected the small number of laboratories capable of making high sensitivity measurements of both uranium and plutonium.

In addition to the blind samples, the SRM's U-100, U-500, and U-900 were sent to all participants in order to assess the linearity of individual measurement systems. Standards were also provided to allow for external normalization of isotopic fractionation by the participating laboratories. The blind samples were gravimetrically prepared from SRM's: the spike SRM's 993 (^{235}U) and 995 (^{233}U) and assay SRM 960 (natural U) were used to prepare the uranium samples; the spike SRM 996 (^{244}Pu) and assay SRM 949e (^{239}Pu) were used to prepare the plutonium samples. By using SRM's to prepare the blind samples, reference values could be assigned with uncertainties calculable from the uncertainties of the individual SRM's. The dominant contribution to the uncertainty of the isotope reference values of the blind samples was the uncertainties in the assays of the spikes, since weighing uncertainties and isotopic composition uncertainties were negligible. Beads containing uranium, beads containing plutonium, and beads containing both uranium and plutonium were prepared, distributed, and analyzed as part of the round robin.

A number of generalized conclusions can be made concerning the resin bead sample loading technique as a result of this round robin: (1) the technique is convenient for shipping, handling, and inventorying very small amounts of uranium and plutonium; (2) a few nanograms of U and Pu can produce a signal intensity adequate for making precise measurements of major isotopes; and (3) laboratories familiar with handling small samples can routinely use this technique. The median accuracy for major isotopic measurement was +0.10 percent; the accuracy of 90 percent of the measurements was between -0.35 percent and +0.85 percent of the reference value; 50 percent of the measurements ranged between ±0.15 percent of the reference values. Isotopic fractionation control was concluded to be a major source of imprecision, and calibration of isotopic fractionation was the major source of inaccuracy for both uranium and plutonium. The results of the round robin were comparable to other blind studies using conventional instrumentation and methodology, such as IDA-72.

24. Standard Reference Materials (14306 and 14307)

B. I. Diamondstone

The analysis and certification of Standard Reference Materials (SRM's) has again been a major part of the total scientific effort of this Division. The fiscal resources for work leading to the issuance of SRM's falls into two categories; STRS--Scientific and Technical Research Services and WCF--Working Capital Funds. The efforts in these two areas account for about 25 percent of the total working budget of the Division with input being provided by the entire scientific staff.

This year, five different research projects were funded by the Office of Standard Reference Materials under the STRS program. The STRS portion of the funding is intended for the preliminary research necessary to develop the methodologies required for the actual production of SRM's. On the other hand, the WCF projects are those which result in the actual certification for chemical composition of a marketable standard. This year, analyses were carried out on more than 75 different SRM's covering a variety of matrices including metals, fossil fuels, nuclear materials, and biologicals. In some cases, each certification can involve 20-30 individual analyses on each potential SRM.

One important accomplishment this year has been the application of recently acquired methodologies for the accurate determination of sulfur in a number of SRM's. Using isotope dilution mass spectrometry and ion chromatography, sulfur has been determined in coal and fuel oil SRM's at four and six concentration levels, respectively. In the area of health and environmental standards, work has continued on the certification of important elements in a variety of SRM's such as Mercury in Water, Citrus Leaves, Bovine Liver, Urban Dust/Organics, and Trace Metals on Filters. Additionally, work has begun leading to the certification of two important future SRM's, Urine and Powdered Milk which will be analyzed for a large number of trace and major constituents.

About 40 percent of the budget allocated for Standard Reference Materials goes towards acceptance testing, homogeneity determination, and eventual certification of both trace and major constituents of a large number and variety of metals. The importance of this area of effort is best illustrated by the fact that nearly 10,000 units of metal SRM's have been sold through the first eight months of FY 82.

The SRM's on which work was carried out this year and the STRS research projects, along with the relative effort in staff-years (SY), are shown in Tables 12 and 13.

Table 12. WCF Work Carried Out on Standard Reference Materials.

Division 551, FY 82

SRM Number	Title	Effort, SY
950b	Uranium Oxide	0.1
U020a, U005a, U030a	Uranium Isotopics	.8
2682, 2683, 2684, 2685	Sulfur in Coals	.6
1622b, 1621b, 1620a, 1619, 1623a, 1624a	Sulfur in Fuel Oils	.4
1244, 1245, 1246, 1247, 864, 865, 866, 867	Inconels and Incalloys	.8
1225, 1226, 1173, 1223, 1134, 1254, 125b, 36b, C1285, C1285a, 1270, 1270a	Low Alloy Steels	1.2
1641b, 1642b	Mercury in Water	0.2
1566, 1567, 1568, 1572, 1573, 1575, 1577a, 1646	Trace Elements in Botanicals	1.0
930d	Glass Filters for Spectrophotometry	0.2
2670, 2671a, 2672a	Trace Elements in Urine	.6
83d, 40b	Primary Chemical Standards	.3
1581	Chlorine in PCB's	.1
1549	Trace Elements in Powdered Milk	.3
2676b	Trace Metals on Filters	.4
C1231, C1232, C2400-C2402	High Alloy Cast Steels	.3
C1290-C1292, 334, 122h	High Alloy Cast Irons	.3
C1251-C1253	Copper Benchmarks	.2
1643a	Trace Elements in Water	.1
1649	Trace Elements in Urban Dust/Organics	.1
371g, 1620a, 143c	Sulfur 32/34 Isotope Ratio Standards	.2
		8.0

Table 13. STRS Projects Underway.

Division 551, FY 82

Task	Description	Effort, SY
Measurement of pH	Complete development of methods for measurement of pH in preparation for renewal of existing SRM's.	0.8
Radiochemical and Instrumental Background Reduction	Develop facilities and methodology for increasing the sensitivity of elements such as As, Sb, Se, Cr, and Mo in biological and environmental SRM's using activation analysis.	.4
Gases in Metals	Re-establish procedures for the bomb distillation Kjeldahl technique for nitrogen determinations and procure equipment to perform analysis of oxygen, nitrogen, and hydrogen in complex metal matrices.	.4
Gas Isotope Dilution Mass Spectrometry	Establish ID/MS methodology aimed at determining carbon, hydrogen, oxygen, nitrogen, and sulfur in various SRM matrices.	.6
Ultratrace Analyses by High Sensitivity Pulse Counting Mass Spectrometry	Develop procedures aimed at providing ultratrace level elemental determinations for V, Ag, Cd, U, Sn, and Si in a variety of SRM matrices.	.6
		2.8

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Heald, E. F. and Moore, L. J., "Thermodynamic and Kinetic Studies of Isotopic Fractionation in the MFTIS," submitted for publication.

Kingston, H. M., Cronin, D. J., and Epstein, M. S., "An Examination of the MCC-1 Leach Method: Experimental Technique," submitted for publication.

Kingston, H. M., Greenberg, R. R., Beary, E. S., Hardas, B. R., Moody, J. R., and Rains, T. C., "The Characterization of the Chesapeake Bay: A Systematic Analysis of Toxic Trace Elements," submitted for publication.

Marinenko, G., Koch, W. F., and Etz, E. S., "High Precision Coulometric Titration of Uranium," submitted for publication.

Messman, J. D., Epstein, M. S., Rains, T. C., and O'Haver, T. C., "Performance Characteristics of a Continuum-Source Echelle Wavelength Modulated Atomic Absorption Spectrometer," submitted for publication.

Moore, L. J., "The Highly Precise and Accurate Measurement of Neodymium and Samarium Isotope Ratios," submitted for publication.

Moore, L. J. and Murphy, T. J., "High Accuracy Barium Isotope Ratio Measurements and Isotope Dilution Applications to Standard Reference Materials," submitted for publication.

Pella, P. A. Kingston, H. M., Sieber, J. R,, and Feng, L., "X-Ray Spectrometric Analysis of NBS SRM Bovine Liver and Pine Needles After Separation and Preconcentration on Cation Exchange Resin Filters," submitted for publication.

Yaffe, Y., Flessel, C. P., Wesolowski, J. J., del Rosario, A., Guirguis, G. N., Martias, V., Gramlich, J. W., Kelly, W. R., DeGarmo, T. E., and Coleman, G. C., "Identification of Lead Sources in California Children Using the Stable Isotope Ratio Techniques," submitted for publication.

2. Talks

Fassett, J. D. and Kelly, W. R., "The Mass Spectrometric Analysis of Uranium and Plutonium Loaded Anion Exchange Resin Beads: An Interlaboratory Round Robin," 25th Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 7, 1981.

Koch, W. F., "Simulated Precipitation Reference Materials: Measurement of pH and Acidity," ASTM Symposium on Sampling and Analysis of Rain, Philadelphia, PA, October 7, 1981. Invited

Lindstrom, R. M., "Compositional Analysis of Solar-Grade Silicon," 160th Meeting of the Electrochemical Society, Denver, CO, October 12, 1981. Invited

Rains, T. C., "State of the Art of Atomic Absorption Spectrometry," NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, October 18, 1981. Invited

Rains, T. C., Rush, T. A., and Butler, T. A., "New Innovations in Atomic Absorption Spectrometry with Electrothermal Atomization for Lead in Foods," 95th AOAC Annual Meeting, Washington, DC, October 19, 1981.

Epstein, M. S., "D.C. Plasma/Echelle Spectrometry," NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD October 19, 1981.

Watters, R. L., "ICP Spectrometry," NBS-ADABSE Analytical Chemistry Workshop, National Bureau of Standards, Gaithersburg, MD, October 19, 1981.

Norris, J. A., "Preparation of Ferrous Standard Reference Materials: SRM 1226: A Case History," Iron and Steel Chemists Meeting, Pittsburgh, PA, October 28, 1981.

Epstein, M. S., "Some Unique and Not-So-Unique Applications of Plasmas to Analytical Atomic Spectroscopy," Perkin-Elmer Corporation, Norwalk, CT, November 2, 1981. Invited

Zeisler, R., Harrison, S. H., and Wise, S. A., "Specimen Banking and Trace Analysis," Clinical Pathology Conference Series, Univ. of Maryland Hospital, Baltimore, MD, November 4, 1981. Invited

Barnes, I. L., "Trace Element Analysis State-of-the-Art," Central Ohio Valley Section--ACS, Huntington, WV, November 9, 1981.

Barnes, I. L., "Trace Element Analysis State-of-the-Art," Kawawha Valley Section--ACS, Charleston, WV, November 10, 1981.

Barnes, I. L., "Trace Element Analysis State-of-the-Art," Upper Ohio Valley Section--ACS, Marietta, OH, November 11, 1981.

Barnes, I. L., "Trace Element Analysis State-of-the-Art," Northern West Virginia Section--ACS, Morgantown, WV, November 12, 1981.

Barnes, I. L., "The Atomic Weights of the Elements," Chemistry Dept., West Virginia University, Morgantown, WV, November 12, 1982.

Barnes, I. L., "Trace Element Analysis State-of-the-Art," Western Maryland Section--ACS, Cumberland, MD, November 13, 1981.

Moody, J. R., "Applications of High Precision Davies-Gray Titrations to Standards for Safeguards," American Nuclear Society, San Francisco, CA, December 1, 1981. Invited

Moody, J. R., "The Sampling, Handling, and Storage of Materials for Trace Analysis," Royal Society Symposium on Recent Advances in Analytical Chemistry, London, UK, December 8, 1981. Invited

Rains, T. C., "Inter-Laboratory Quality Control Program and Reference Samples," University of Minnesota's 3rd Annual Midwest Conference on Environmental Laboratory Technology, Minneapolis, MN, December 8, 1981. Invited

Rains, T. C., "Atomic Absorption Analysis of Hazardous Waste Materials," University of Minnesota's 3rd Annual Midwest Conference on Environmental Labortory Technology, Minneapolis, MN, December 9, 1981. Invited

Moody, J. R., "Trace Analysis with Limited Resources," Analytical Symposium, Harwell Laboratories, UK, December 11, 1981. Invited

Barnes, I. L., "The Evaluation of Magnetic Stray Fields," National Bureau of Standards, December 12, 1981.

Moody, J. R., "The Use of Isotope Dilution Mass Spectrometry for Accurate Analysis of Reference Materials and Standards," Central Bureau for Nuclear Measurements Analytical Seminar, Geel, Belgium, December 15, 1981. Invited

Moody, J. R., "High Accuracy Trace Analysis by Isotope Dilution Mass Spectrometry," Univ. of Ghent/Institute for Nuclear Science Joint Analytical Seminar, Ghent, Belgium, December 16, 1981. Invited

Epstein, M. S., "Aspects of Quality Control in the Use of a D.C. Plasma for the SRM Certification Process," Conference on Plasma Spectrochemistry, Orlando, FL, January 4, 1982. Invited

Moody, J. R., "Modification of Laboratories for Safety and Trace Analysis," Laboratory of the Government Chemist Engineering Staff Meeting, London, UK, January 6, 1982. Invited

Marinenko, G., "Absolute Electroanalytical Measurements at NBS," Seminar at IBM Instruments, Inc., Danbury, CT, February 26, 1982. Invited

Epstein, M. S., "Atomic Absorption Spectroscopy," ACS Short Course, Pittsburgh Conference, Atlantic City, NJ, March 6, 1982.

Rains, T. C., "Atomic Absorption Spectrometry," ACS Short Course, Pittsburgh Conference, Atlantic City, NJ, March 6, 1982.

Marinenko, G., "Absolute Electroanalytical Measurements at NBS," Seminar at Pennsylvania State University, March 19, 1982. Invited

Powell, L. J., "The Atomic Weight of Silver and a New Value for the Faraday Constant," U.S. Naval Academy, Department of Chemistry, Annapolis, MD, March 23, 1982. Invited

Epstein, M. S., "Some Applications of Dye Lasers to Analtyical Atomic Spectroscopy," Villanova University, Dept. of Chemistry Seminar, Villanova, PA, March 30, 1982. Invited

Rains, T. C., "State of the Art of Sample Preparation for Environmental Analyses," Dept. of Chemistry, Murray State University, Murray, KY, April 6, 1982. Invited

Rains, T. C., "Characterization of Standard Reference Materials," Penwalt Corporation, Calvert, KY, April 7, 1982. Invited

Rains, T. C., "Analytical Chemistry at the National Bureau of Standards," Western Kentucky University, Dept. of Chemistry Seminar, April 8, 1982. Invited

Shideler, R. W., "Operational Amplifiers as Used in Modern Measuring Instrumentation," National Bureau of Standards Group Seminar, Gaithersburg, MD, April 12, 1982.

Rains, T. C., "The State of the Art of Sample Preparation for Atomic Absorption and Emission Spectrometry," Penn-York Section of SAS, Corning, NY, April 27, 1982. Invited

Kingston, H. M. and Cronin, D. J., "An Examination of the MCC-1 Leach Test Method, Part II: Experimental Technique," 2nd Semiannual Workshop on the Leaching Mechanisms of Nuclear Waste Forms, Gaithersburg, MD, May 1982. Invited

Cronin, D. J. and Kingston, H. M., "An Examination of the MCC-1 Leach Test Method, Part III: Comparison of Glass Compositions," 2nd Semiannual Workshop on the Leaching Mechanisms of Nuclear Waste Forms, Gaithersburg, MD, May 1982. Invited

Rains, T. C., "State of the Art of Sample Preparation for Atomic Spectroscopy," 2nd Annual Multi-Discipline Symposium, Chicago Section of SAS, Chicago, IL, May 3, 1982. Invited

Zeisler, R., Harrison, S. H., and Wise, S. A., "Analysis of Human Liver Specimens in the U.S. Pilot National Environmental Specimen Bank Program," Intern. Workshop on Environmental Specimen Banking and Monitoring as Related to Banking, Saarbrucken, FRG, May 12, 1982. Invited

Norris, J. A., "Line Interferences in Optical Emission Spectroscopy," Lehigh Valley SAS, Reading, PA, May 14, 1982.

Zeisler, R., "Recent Experience in the Analysis of Specimens in the U.S. Pilot NESB Program," 6th U.S./German Bilateral Meeting on Specimen Banking, Neuherberg FRG, May 17, 1982. Invited

Zeisler, R., "Neutron Activation Analysis Procedures Applied to Human Liver Analysis," 6th U.S./German Bilateral Meeting on Specimen Banking, Neuherberg, FRG, May 17, 1982. Invited

Norris, J. A., "Line Interferences in Optical Emission Spectroscopy," Technical Committee on Chemical Analyses AISI, Boston, MA, May 19, 1982.

Kelly, W. R. and Paulsen, P. J., "The Isotopic Analysis of Sulfur," Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, June 4, 1982. Invited

Moody, J. R., "Applications of Clean Room Technology to Inorganic and Organic Trace Analysis," Philip Morris Research Center, Richmond, VA, June 4, 1982.

Garner, E. L., Gills, T. E., and Moore, L. J., "The Current Status and Future Role of NBS SRM's in the Nuclear Energy Community," ASMS, Honolulu, HI, June 8, 1982. Invited

Greenberg, R. R., Kingston, H. M., and Rains, T. C., "Trace Elemental Characterization of the Chesapeake Bay Water Column," American Nuclear Society Meeting, Los Angeles, CA, June 8, 1982. Invited

Kelly, W. R. and Paulsen, P. J., "The Determination of Microgram Quantities of Sulfur by Thermal Ionization Mass Spectrometry," 30th Annual Conference on Mass Spectrometry and Allied Topics sponsored by American Society for Mass Spectrometry, Hilton Hawaiian Village, Honolulu, HI, June 9, 1982. Invited

Moore, L. J., "Laser Mass Spectrometry for the Production and Measurement of Inorganic Ions," ASMS, Honolulu, HI, June 9, 1982.

Zeisler, R. and Greenberg, R. R., "Procedure for the Determination of the Platinum Baseline in Biological Materials," American Nuclear Society Annual Meeting, Los Angeles, CA, June 9, 1982. Invited

Zeisler, R. and Harrison, S. H., "Distribution of Pollutant and Essential Elements in Human Livers," American Nuclear Society Annual Meeting, Los Angeles, CA, June 9, 1982.

Fleming, R. F. and Lindstrom, R. M., "Limitations on the Accuracy of Sulfur Determination by NAA," American Nuclear Society Annual Meeting, Los Angeles, CA, June 10, 1982.

Norris, J. A., "NBS Standard Reference Materials," Northwest ICP Users Conference, Seattle, WA, June 16, 1982.

Kelly, W. R. and Paulsen, P. J., "The Isotopic Analysis of Sulfur," Dept. of Chemistry, Arizona State University, Tempe, AZ, June 18, 1982. Invited

Moore, L. J., "Current Trends in Inorganic Mass Spectrometry," Hitachi Ltd., Naka Works, Ibaraki-ken, Japan, June 22, 1982. Invited

Moody, J. R., "New Developments in Laboratory Design in the USA," Lab Design 82, International Conference on Laboratory Design and Servicing, London, UK, June 23, 1982. Invited

Moore, L. J., "Current Trends in Inorganic Mass Spectrometry and Isotope Metrology," Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan, June 23, 1982. Invited

Moore, L. J., "Some New Measurement Concepts in High Sensitivity Mass Spectrometry," Hamamatsu T.V. Co., Hamamatsu City, Japan, June 24, 1982. Invited

Moore, L. J., "Recent Advances in Inorganic Mass Spectrometry and Analytical Chemistry," Toyota Motor Corporation, Toyota City, Japan, June 25, 1982. Invited

Moore, L. J., "Highly Sensitive and Selective Stable Isotope Measurements Using Laser Mass Spectrometry," 5th Intern. Conf. on Geochronology, Cosmochronology and Isotope Geology, Nikko National Park, Nikko, Japan, June 29, 1982.

Kingston, H. M., "The Leach Testing Evaluation of Simulated Nuclear Waste Glasses: Can It Be Done Precisely?" Division Seminar, National Bureau of Standards, Gaithersburg, MD, July 1982.

Rains, T. C., "Application of AAS for Trace Elemental Analysis in Biological Fluids," Center for Clinical Research, London, England, July 12, 1982. Invited

Rains, T. C., "Atomic Absorption Spectrometry: A Challenge in the Analysis of Environmental and Biological Materials," First Biennial National Atomic Spectroscopy Symposium, Sheffield, England, July 13, 1982. Invited

Rains, T. C. and Butler, T. A., "Determination of Chromium Species in Environmental Samples by Atomic Absorption Spectrometry," First Biennial National Atomic Spectroscopy Symposium, Sheffield, England, July 13, 1982.

Norris, J. A., "Quantitative and Semiquantitative Analyses, Statistics, and Direct Reading Spectrochemical Analysis," Modern Industrial Spectroscopy, Arizona State University, Tempe, AZ, August 2, 1982.

Fassett, J. D., Travis, J. C., Moore, L. J., and Lytle, F. E., "Resonance Ionization of Mo, V, and Re Vapor Phase Atoms," Microbeam Analytical Society Annual Meeting, Washington, DC, August 11, 1982. Invited

Fassett, J. D., Travis, J. C., Moore, L. J., and Lytle, F. E., "Some New Approaches to the Formation and Measurement of Metal Ions," 9th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 1982.

Rains, T. C., "Atomic Absorption Spectrometry," ACS Short Course, National ACS Meeting, Kansas City, MO, September 11, 1982.

Paulsen, P. J. and Kelly, W. R., "Analysis of Sulfur in NBS Standard Reference Materials by Thermal Ionization Mass Spectrometric Isotope Dilution," National ACS Meeting, Kansas City, MO, September 14, 1982.

Powell, L. J., Brletic, K. A., and Garner, E. L., "A High Sensitivity Method for the Determination of Chromium by Isotope Dilution Mass Spectrometry," 9th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 20, 1982. Invited

Zeisler, R., "Bio-monitoring for Environmental Health: Use of INAA, RNAA, PGAA, and Role of Specimen Banks," IAEA Advisory Group Meeting on Nuclear Techniques in Environmental Health Studies of Mineral Pollutants, Athens, Greece, September 20, 1982. Invited

Epstein, M. S., "Multi-Element Characterization of Simulated Nuclear Waste Leachates Using a D.C. Plasma," 9th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 21, 1982. Invited

Rains, T. C., Rush, T. A., and Butler, T. A., "Improved Precision and Accuracy by Electrothermal Atomization/Atomic Absorption Spectrometry in Environmental Samples," 9th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 22, 1982.

Moody, J. R., "The Preparation and Certification of Environmental Standard Reference Materials," 9th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 23, 1982. Invited

Rains, T. C. and Powell, L. J., "Sample Preparation Workshop," 9th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 24, 1982. Invited

3. 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
- Secretary, IUPAC, Commission on Atomic Weights, Subcommittee for Assessment of Isotopic Abundances

Robert W. Burke
- Member, ASTM D-34, Waste Disposal
  - ASTM E-03, Chemical Analysis of Metals

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

Michael S. Epstein
- Member, ASTM D-19, Water
  - Board of National Correspondents, ICP Information Newsletter
  - Editorial Advisory Board, Progress in Analytical Atomic Spectroscopy
- Assistant Program Chairman, Federation for Analytical Chemistry and Spectroscopy Societies
- Chairman-Elect, 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, Organization and Planning Committee, the Fourth International Conference on Neutron Transmutation Doping of Semiconductors
  - Committee on Accelerator-Based Neutron Research at NBS Center
  - Colloquium Committee

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 Element 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

William F. Koch
- Member, ASTM D-19, Water
  - ASTM D-19.02, General Specifications and Technical Resources
  - ASTM D-19.05, Inorganic Constituents in Water
  - ASTM D-22, Air
- Chairman, Teller's Committee, Chemical Society of Washington

John K. Langland
- Member, NBS Electronics Storeroom 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
        ASTM D-19.01, Saline in Brackish Waters
        ASTM D-19.05, Inorganic Constituents in Water
        ASTM D-19.05.03.06, Ozone
    Chairman, ASTM D-19.05.04.03, Voltammetry
        ASTM D-19.09.01.04, Chlorine in Saline Water
        ASTM D-19.09.06, Redox Potentials
        ASTM D-19.09.07, pH in Saline Water
        National Capital Section of the Electrochemical Society
        Blum Award Arrangements, Committee 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

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-02.01, Fundamental Practices
        ASTM E-02.02, Statistics
        ASTM E-02.04, Sampling and Standards
        ASTM E-02.06, Lead, Tin, Zinc
        ASTM E-02.07, Aluminum
        ASTM E-02.08, Refractory Metals
        ASTM E-02.09, Ferrous
        ASTM E-02.10, Miscellaneous Non-Metallic Materials
    Secretary, ASTM E-02, Emission Spectroscopy
    Lecturer, Annual Short Course, "Modern Industrial Spectroscopy," Arizona State University, Tempe, AZ

Lura J. Powell
    Member, Audit Committee, Chemical Society of Washington
        Program Committee, American Society for Mass Spectrometry
    Chairman, Committee on Isotope Ratio Measurements, American Society for Mass Spectrometry

Theodore C. Rains
- Member, Proposal Evaluation Committee for National Science Foundation
  - AOAC Committee on Automated Methods
  - 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
- President, Society for Applied Spectroscopy
- Director, Professional Development Program for the Baltimore-Washington Section of the Society for Applied Spectroscopy
- Professor-in-charge, ACS Short Course on "Atomic Absorption Spectroscopy"
- Task Force Leader in 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

Robert L. Watters, Jr.
- Assistant Program Chairman, Federation for Analytical Chemistry and Spectroscopy Societies

Rolf L. Zeisler
- Member, IAEA Advisory Group on Nuclear Techniques in Environmental Health Studies of Mineral Pollutants
- Chairman, Trace Element Analysis Committee, Biomedical Division, American Nuclear Society

4. Other

a. Seminars

October 16, 1981 - Robert E. Michaelis, Office of Standard Reference Materials, National Bureau of Standards, Washington, DC, "Testing and Characterization of SRM's"

December 3, 1981 - Michael S. Epstein, Atomic & Molecular Spectrometry Group, Inorganic Analytical Research Division, National Bureau of Standards, Washington, DC, "Problems (and a Few Solutions) Using a D.C. Plasma/Echelle Spectrometer for Analytical Atomic Spectroscopy"

January 28, 1982 - William R. Kelly, Mass Spectrometry Group, Inorganic Analytical Research Division, National Bureau of Standards, Washington, DC, "The Determination of Sulfur by Thermal Ionization Mass Spectrometry"

February 18, 1982 - James R. Vogt, University of Missouri on IPA with Inorganic Analytical Research Division, National Bureau of Standards, Washington, DC, "Activation Analysis of Obsidian"

March 16, 1982 - G. L. Fisher, Occupational Health and Safety Division, National Bureau of Standards, Washington, DC, "Ease in the Workplace"

April 15, 1982 - William P. Reed, Office of Standard Reference Materials, National Bureau of Standards, Washington, DC, "Preparation and Certification of Standard Reference Materials"

May 13, 1982 - Louis Brown, Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC, "Accelerator Mass Spectrometry Applied to Be-10"

June 8, 1982 - P. Goel, Indian Institute of Technology, "Non-Magmatic Origin of Iron Meteorites"

July 8, 1982 - Howard M. Kingston, Mass Spectrometry Group, Inorganic Analytical Research Divison, National Bureau of Standards, Washington, DC, "The Leach Testing Evaluation of Simulated Nuclear Waste Glasses: Can It Be Done Precisely?"

III. Organic Analytical Research Division

Harry S. Hertz, 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 six groups organized along functional lines: Bioanalytical Techniques, Electrochemistry, Gas Chromatography, Liquid Chromatography, Mass Spectrometry, and Spectroscopy. During the past year, 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 Division research are utilized by industry, other Federal agencies, public and private institutions, and research programs at the National Bureau of Standards.

The year just completed has been very productive for the Organic Analytical Research Division. During this period 45 publications have been published or are in press in archival journals. A third competence project, Bioanalytical Techniques - The Use of Proteins in Analytical Chemistry, has been added to the research already being carried out in Organic Electrochemistry and the Analysis of Ionization Mechanisms and Ion Structures.

As in past years, our research efforts have been in support of basic organic analytical chemistry, in support of other agency requests and in short term projects performed on a service analysis basis. A major service effort during the past year has been a review of the Environmental Protection Agency Monitoring Study for Organic Chemicals in the Love Canal Area. Although we believe this was an extremely important undertaking, it did impact our abilities to advance our research in the ion structures competence project.

A matter of pride for the Division during the past year was the recognition of Drs. Robert Schaffer and Alexander Fatiadi for their contributions to research in clinical chemistry and synthetic organic chemistry, respectively. Dr. Schaffer was honored with the Roe Award of the Capitol Section of the American Association for Clinical Chemistry and Dr. Fatiadi with the Hillebrand Award of the Chemical Society of Washington.

The results of our research are described in some detail in the group overviews and individual technical reports which follow. Some aspects of this research deserve particular highlighting. We have been most pleased with our initial efforts in the new competence program on Proteins in Analytical Chemistry. Research in two-dimensional electrophoresis has begun and efforts are underway to correlate protein migration with impurities in the sodium dodecyl sulfate used in the electrophoretic system. Also, as part of this research, a collaborative effort has already begun with marine biologists of the National Oceanic and Atmospheric Administration; we are using immunoelectrophoresis to investigate patterns of proteins for species identification in commercial flounder. In our Organic Electrochemistry program, theoretical and experimental studies have been carried out on the diffusion of substances through polymer films bound to electrode surfaces. In a joint effort between the Electrochemistry and Liquid Chromatography Groups, methods for the analysis of nitro-polynuclear aromatic hydrocarbons have been investigated. These compounds are of particular concern due to their potential health hazard and their presence on particulate matter arising from diesel emissions. A novel method has been developed involving reduction of the nitro moiety to an amino function with subsequent, highly sensitive fluorescence detection. This project has been undertaken as a cooperative effort with the Coordinating Research Council, a group representing the automotive, petroleum, and farm equipment industries. In a collaborative effort with the State of California, we have evaluated a round robin material for the analysis of pesticides on soil. We have developed high resolution gas chromatographic methods allowing us to separate greater than 100 chlorinated pesticides and PCB compounds. Research efforts on our combined liquid chromatography/mass spectrometry system have continued with the implementation of our ultrasonic probe for reversed-phase liquid chromatography and applications to the direct analysis of drugs in serum and carboxylic acids in a shale oil process water. With the availability of an advanced pulse programmer for the 400 MHz nuclear magnetic resonance spectrometer initial research has been carried out in heteronuclear two-dimensional NMR. In examinations of tripalmitin, a candidate Standard Reference Material (SRM), proton coupled ^{13}C multiplets have been displayed separately from ^{13}C chemical shift information.

A number of new and challenging SRM's have been certified during the past year. Of particular interest are SRM's for PCB's in oil and for urban air particulate matter. Due to federal regulations governing the declaration of oils as hazardous wastes, based upon their PCB content, it is extremely important that analyses for these widely-used transformer fluids be performed as accurately as possible. This SRM permits an accuracy check on such analyses for the first time. The urban air particulate matter certified for a number of polynuclear aromatic hydrocarbons represents the first solid matrix material certified for its native content of trace organic species. In addition, the human serum SRM has been upgraded through the certification of urea content and through an information value for total protein content. Finally, the certification of a drinking water SRM with certified concentrations for common halocarbons is currently underway. This SRM has been challenging both from the preparation and analysis standpoints.

During the past year, the toxic chemicals handling laboratory, a major safety feature for the Center for Analytical Chemistry, has been completed. We believe we now have a unique facility for the storage and handling of toxic chemicals. We invite visits to this laboratory and would be happy to discuss interesting aspects of the design of this laboratory. We are currently completing the design of a new gas chromatography laboratory and plan on beginning construction early in the coming year.

In keeping with the research planning which we have been actively doing for the past several years, we anticipate pursuing some very exciting research areas during the coming year. In the bioanalytical competence area, investigations will begin on the modification of proteins to tailor them as markers for our two-dimensional electrophoretic system and on the examination of the silver staining process for visualizing proteins separated by gel electrophoresis. We will be examining the "diffusional" current-time response of polymer film modified electrodes as part of our continuing research on chemically modified electrodes. We will be furthering our research on the analysis of ion structures through the photodissociation of ions of low internal energy. Research in high resolution chromatography will continue in the areas of isotope dilution gas chromatography, examination of liquid chromatographic retention mechanisms, and multidimensional gas and liquid chromatography. During the coming year, we plan to expand our research efforts in heteronuclear two-dimensional NMR and to explore the potential of this technique.

Finally, as pointed out in last year's annual report, we have made major new thrusts in the application of our research to the areas of organic nutrient analysis and hazardous waste analyses. We have implemented research programs in both these areas and are anticipating worthwhile research results in the coming year.

1. Bioanalytical Group: Overview

A major thrust of the Bioanalytical Group during the past year has been initiation of a competence program in bioanalytical research. The use of proteins in analytical chemistry is a rapidly growing area of interest and offers capabilities not possible with many instrumental methods. We are starting work on developing competence in the use of proteins as analytical reagents and on developing sensitive methods for determining the purity of proteins. Our efforts began by implementing access to a library of specialized reprints whose titles and references were entered into a microcomputer data base. In addition, contacts were made with many research users of two-dimensional electrophoresis (2-DE) in November 1981, at a meeting on 2-DE held at the Mayo Clinic. Laboratory equipment to perform 2-DE was set up and methods were examined for generating gradient polyacrylamide gels, for handling thin (0.7 mm) gels, and for staining and photographing gels. Isoelectric focusing in long (170 mm) tube gels was implemented, with ampholytes from several manufacturers being used.

A study of the effect of the composition of sodium dodecyl sulfate (SDS) preparations on 2-DE separations was begun with ten different lots of the detergent. The relative purity of the materials was examined by gas chromatography after hydrolyzing the sulfate esters to free the long-chain (C_{10}, C_{12}, C_{14}) alcohols. The banding patterns of several proteins versus the relative composition of the SDS preparations are being correlated.

A modest joint research effort using electrophoresis was started with the Sandy Hook Marine Laboratory, NOAA, Department of Commerce, to investigate patterns of proteins in commercial flounder. Immunoelectrophoresis was used, the antiserum being provided by the National Fish Health Research Laboratories, Department of Interior.

Coordinating work leading to the certification of SRM 1599, Anticonvulsant Drug Level Assay Standard, was completed during this year. Release of that SRM is due in the last quarter of FY 82. Measurements leading to the certification of the total protein content of SRM 909, Human Serum, were made by an accepted biuret method for which SRM 927, Bovine Serum Albumin, served as the primary protein standard.

A major continuing activity is the investigation and implementation of minimal-error-prone, wet-chemical steps into our ID/MS methods, i.e., for samplings, spikings, and analyte isolations that are performed before the GC/MS measurements. For our serum-urea method, we synthesized ^{18}O-urea to replace the commercially available $^{15}N_2$-urea which we used initially as the internal standard. Its substitution by ^{18}O-urea obviates possible isotope-effects in the N-C bonds that form in converting the urea into volatile 5-O-methyluracil. Also we found improved conditions for obtaining the derivative from urea. For our serum-creatinine ID/MS method (for which we synthesized methyl-labeled $^{2}H_3$-creatinine to avoid an analogous isotope effect that could arise on using commercially available ^{15}N-labeled creatinine), we are exploring an alternative wet-chemistry process for effecting separation of the creatinine. Previously, spiked samples were ultrafiltered to remove most of the protein, and the creatinine was then separated by HPLC from creatine and other substances in the sample. Now we are separating the creatinine by LC using ion-exchange, the effluent containing the creatinine is freeze-dried, and the creatinine is extracted from the residue. This approach is very simple to carry out and appears to be subject to fewer sources of error.

In collaboration with the Mass Spectrometry Group, the urea ID/MS method was used to determine definitive values for urea in SRM 909 and also in a series of serum pools. The urea levels in the latter were also determined by a study group of the AACC Standards Committee using a candidate reference method. The absence of bias of the latter method was established by comparison. Manuscripts on the ID/MS method and the comparison of the reference method with the ID/MS method are being prepared for publication.

Our paper on a multilaboratory-evaluated serum-sodium reference method has been published in Clinical Chemistry. We also co-authored a publication under the AACC Standards Committee on the interlaboratory testing of a candidate reference method for uric acid.

A joint study with the Electrochemistry Group has been published in Angewandte Chemie on the behavior of oxocarbon salts of croconic acid and its dicyanomethylene derivatives. These compounds in *N*,*N*-dimethylformamide undergo two consecutive, reversible, one-electron transfers to produce stable radical ions and neutral croconates.

In the coming year, we will continue investigations on the effect of materials purity on 2-DE separations of selected proteins. We will also study silver staining of gels to improve the sensitivity of detection. Several proteins will be studied in depth, with the objective of selectively modifying their charge and molecular weight to provide markers for the 2-DE system.

We expect to be able to complete our ID/MS work on creatinine and to complete the development of an ID/MS method for total triglycerides.

Robert Schaffer, Group Leader; Alex Cohen, Alexander J. Fatiadi,
Dennis J. Reeder

2. Electrochemistry Group: Overview

The competence building program in organic electrochemistry has made good progress this year and we have begun applying the results of our research to NBS programmatic areas. During the fourth year of this effort, full staffing has been maintained and most of the major pieces of equipment are now operational, although some needs still exist for instrumentation to achieve our planned research goals.

Our activities are now focused on the study of organic redox reactions using state-of-the-art electrochemical techniques: cyclic voltammetry and rotating ring-disk electrochemistry; hybrid techniques such as spectroelectrochemistry and liquid chromatography with electrochemical detection; the preparation, study, and application of chemically modified electrodes; and the theoretical modeling of electrochemical processes in support of the Group research areas.

In the area of spectroelectrochemistry, copper and iron bleomycin complexes are being studied in an effort to define more clearly the role of the metal ion in the mechanism of bleomycin action. Spectroelectrochemistry provides qualitative information concerning the identity of solution species and quantitative data such as the formal redox potential and number of electrons involved in the redox process. From data obtained by cyclic voltammetry, coulometry and atomic absorption spectroscopy, a reduction mechanism for Cu(II) bleomycin is proposed which involves the subsequent dissociation of the Cu(I) complex, and reduction of the free Cu(I) to copper metal.

Iron bleomycin exhibits quasi-reversible behavior at glassy carbon electrodes and its spectroelectrochemical behavior was consequently studied in a specially constructed optically transparent electrode cell with a reticulated vitreous carbon working electrode which exhibits thin-layer behavior. The spectroelectrochemical data were analyzed by means of Nernst plots to give the n value and formal potential for the redox process.

Cyclic voltammetry, chronocoulometry, and spectroelectrochemistry are being used to examine electrode reactions of the laser dye 4-[2-(5-phenyloxazolyl)]-1-methylpyridinium tosylate. We are attempting to elucidate the nature of the process(es) responsible for the complex electrochemical behavior of this compound in aqueous solutions. In non-aqueous solution, the complex anodic behavior observed in aqueous solutions disappears, and both reduction and oxidation appear to be diffusion controlled.

Another project underway is an investigation of the spectroelectrochemistry of cyanine laser dyes. Using the cationic dye 1,1'-diethyl-4,4'-carbocyanine iodide, we have examined the reduction of the cation to a radical molecule in dimethyl formamide at a gold electrode. Cyclic voltammetry indicates a one-electron reduction that is both chemically and electrochemically reversible. Spectroelectrochemistry shows a virtually quantitative conversion from the cation which is accompanied by a sharp visual color change from azure blue to violet. Furthermore, the radical product appears to be exceptionally stable, undergoing no obvious decomposition over several hours in a thin-layer cell.

A series of experiments were undertaken to clarify the role of the anion in surface-enhanced Raman scattering (SERS) measurements involving the N-methylpyridinium cation (NMP^+) and to identify the actual surface species observed in such experiments. We studied the effects of varying the anion, pH, and electrochemical potential, performed competition experiments in which both pyridine and NMP^+ were present in the electrolyte, and compared the ordinary Raman spectrum of the solid silver-pyridine complex, $Ag(py)_2NO_3$, with the various SER spectra obtained. By these experiments, we demonstrated that different pyridine/NMP^+ species are responsible for the observed spectra. In addition, it appears that surface-induced and/or photochemical reactions may produce species not originally present in the sample solution.

Nitro-polycyclic aromatic hydrocarbons are a class of highly mutagenic compounds found in the environment and for which analytical methods are currently needed. In collaboration with the Liquid Chromatography Group, the detection of nitro-aromatic compounds by electrochemical methods has been approached in several ways. The direct reductive detection approach is complicated by the requirement of atmospheric oxygen exclusion and thus the detection limits found were somewhat poorer than some alternative detection methods. Considerable work was devoted to a scheme for coulometric conversion of the nitro to an amino group for subsequent detection. Since only the amine products were suitable for fluorescence detection and these were generated inefficiently, this conversion route was abandoned. A simpler approach to the nitro-to-amino conversion was achieved using a Jones reductor. The Jones reductor column is inserted in the outlet stream after the reversed-phase column but in front of the fluorescent or amperometric detectors. This approach resulted in an efficient and quantitative conversion.

Chemically modified electrodes may provide sensors which will allow the selective and sensitive detection of organic analytes (e.g., organohalides). Chemical modification by polymer films offers the advantages of inherent chemical and physical stability, incorporation of large numbers of catalytic sites, and relatively facile electron transport across the film. We have followed two approaches in polymer film electrode fabrication: electrochemical initiated polymerization and spin-dip coating. These two approaches allow a much greater degree of flexibility in polymer film type, thickness, and morphology. However, the most important aspect is that we are given a greater latitude in the subsequent mode of catalyst immobilization.

Another area of investigation is the behavior of charged or uncharged film penetrants. The ultimate catalytic efficiency of these polymer film electrodes will depend to a great extent on the influx of these substrate molecules across the film interface. We have started both theoretical and experimental investigations, which we hope will shed light on the factors that influence diffusion of substrate molecules in the polymer films.

Polymer films of $[Ru^{II}(bipy)_2(4\text{-}VP)_2]\cdot 2PF_6$ (where bipy is bipyridine and VP is vinyl pyridine) have been obtained via electrochemical initiation of an anionic polymerization of the vinyl monomer. These films have shown very facile electron transfer through the film and catalytic oxidation of organic carboxylates. We have also utilized these $Ru^{II}(bipy)_2(4\text{-}VP)_2$ polymer films in the evaluation of the role and relative influence that migration plays in the "diffusional" current-time response of these polymer film electrodes.

This area of research is still being pursued and the soon-to-be-completed computerized equipment will greatly facilitate this study.

The immobilization of cationic catalysts within a cationic exchange polymer has been demonstrated. The immobilization scheme consists of two parts: spin-dip coating of the polymer onto the electrode and then subsequent ion exchange of the cation of interest. These films have shown electrochemical response with cations such as methyl viologen, methylene blue, and $Ru^{II}(bipy)_3$.

In electrochemical studies using polymer-coated electrodes, there are indications that the transport of the charged electroactive species through the polymer layer may take place not only by diffusion, but also by electromigration. We have made a theoretical analysis of chronoamperometry using polymer-coated electrodes. Equations were developed for the concentration distributions of the charged electroactive species and for the current as a function of time. Using the curves generated by these equations, it is now possible to estimate the fraction of the total current due to electromigration and to determine whether the migration current adds to or opposes the diffusion current. Such information is vital to our understanding of charge transport processes in polymer-modified electrodes.

Our plans for the coming year call for continued research on several of the above projects with expanded efforts in the area of chemical modification of electrodes as selective organic sensors. Because of the loss of our two full-time spectroelectrochemists (one completing her graduate studies at NBS and the other her tenure as a post-doctoral fellow), research in this area of our program will be reduced. We have added a new graduate student in the spectroelectrochemistry area. Our basic studies are expected to be rapidly adapted to address the analytical needs of the Center.

Richard A. Durst, Group Leader; Elmo A. Blubaugh, Jr., Kathryn A. Bunding, Richard T. Burke, Mary Lou Fultz, William A. MacCrehan, Gwendolyn S. Marbury, William T. Yap

3. Gas Chromatography Group: Overview

Three areas of basic analytical research have been explored by the Gas Chromatography Group during the past year. First, our effort in combined gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR) has been continued and two additional Group members have been trained on the instrumentation. The GC/FTIR was used to identify polychlorinated biphenyls (PCB) congeners present in individual liquid chromatographic fractions of Aroclors 1242, 1254, and 1260. In addition, several more PCB spectra were obtained and added to our spectral search library. Second, a collaborative study was initiated with the Center for Fire Research (CFR) in which trace organic analysis was applied to residues of electrical insulation after exposure to fire conditions. Chemical markers were sought as indicators of electrically initiated fires. While such markers were not specifically identified, other valuable data on organic residues were collected. Third, a multi-year program was started, again with the CFR, to monitor organic emissions resulting from wood combustion. A prototype sampling system was built by members of the Gas

Chromatography Group to collect both gaseous and condensed organics. Gas chromatographic profiles of phenolic compounds emitted from wood burning stoves were constructed as a function of position and temperature within the exhaust stack.

As in past years, the Group has been actively involved in the Standard Reference Material program. We have participated in the certification analyses for the following materials:

1. Polychlorinated Biphenyls in Oil, SRM 1581 - Completed analyses of Aroclors 1242 and 1260, each in motor and transformer oil matrices
2. Washington Urban Dust, SRM 1649 - Completed gas chromatographic analyses for a selected number of polycyclic aromatic hydrocarbons
3. Petroleum Crude Oil, SRM 1582 - Dibenzothiophene analyses completed and analyses for phenols are underway
4. Organics in Drinking Water, SRM 1639 - Ampouling has been completed and analyses for carbon tetrachloride, trichloroethane, bromodichloromethane, dibromochloromethane, tetrachloroethylene, bromoform, chloroform, and bromotrichloromethane are underway
5. Ethanol in Wine, SRM 1590 - Recertification of ethanol content completed

The ampouling of the Drinking Water SRM required the development of a packaging technique to maintain the physical integrity of the SRM and also prevent losses of highly volatile components. The SRM is prepared and delivered to the ampouling machine from a collapsible Teflon bag, thermostated to 0 °C.

A gas chromatographic method has been developed for analysis of pesticides in human tissues. Using this method, we can quantitate over 100 pesticides and PCB congeners in a single chromatographic run. Using this procedure, a homogeneity study of a human liver tissue homogenate was also completed. This pesticide procedure was modified for soil samples and was employed to successfully confirm the pesticide content of a State of California proficiency testing soil sample.

We have prepared and quantitated a number of polychlorinated biphenyl (PCB)-containing oil samples for a joint NBS/ASTM round robin. These samples have PCB contents between 10-300 ppm. Results from the collaborative laboratories are now being collated and reviewed for publication in FY 83.

In collaboration with the Mass Spectrometry Group, another set of marker compounds, to be used by EPA in its Level I Method, has been prepared and stability studies are underway. For a new program with EPA, high-resolution gas chromatography is also being applied to the analysis of ten specified organic compounds added to a natural sludge matrix.

During the past year, a new automated gas chromatograph was obtained and is operating successfully. This unit has been used for overnight unattended analyses. In addition, a state-of-the-art sulfur specific flame photometric detector (FPD) has been procured for the automated gas chromatograph and optimized for petroleum samples. The FPD has been successfully used in the certification of the content of dibenzothiophene in SRM 1582 (34 ± 1 ppm).

Plans for an enlarged gas chromatography laboratory have been prepared. This new facility will provide working space for approximately five chemists and will accomodate ten gas chromatographs and ancillary equipment.

During FY 83 we will continue to pursue our programs in GC/FTIR and combustion modeling. Also, we plan to further our competence in the areas of multidimensional and isotope dilution gas chromatography.

Stephen N. Chesler, Group Leader; Delmo Enagonio, Franklin R. Guenther, Reenie M. Parris, Richard E. Rebbert

4. Liquid Chromatography Group: Overview

The major emphasis of research in the Liquid Chromatography Group continues to be focused in two areas: the development of a clearer understanding of the retention mechanisms involved in normal- and reversed-phase liquid chromatography and the development of selective detection procedures and systems for specific compounds and classes of compounds. The results from these efforts are applied to the determination of individual compounds in complex biomedical, environmental, and food matrices. These research efforts have resulted in 34 publications being co-authored (frequently with members of other groups) by members of the group during the past year.

Specific research accomplishments for the past year include: (1) Investigation of the effect of octadecylsilane (C-18) surface coverage on the relative retention (selectivity) of polynuclear aromatic hydrocarbons (PAH) and sulfur containing polycyclic aromatic compounds. Changes in elution order were often observed as the C-18 surface coverage increased and were greatest for non-planar solutes such as polyphenyl arenes. (2) Development, in collaboration with the Mass Spectrometry Group, of an ultrasonic probe for introducing reversed-phase LC effluents into a mass spectrometric ion source. Although mentioned in concept last year, the operation of the ultrasonic probe was realized during the past year. The LC/MS system was used to measure the concentrations of valproic acid in human serum and aliphatic acids in a shale oil process water. (3) Completion of the development of our gas saturation-HPLC method for measuring vapor pressures in the ambient temperature range. Vapor pressures and heats of sublimation/vaporization were measured for 15 compounds with vapor pressures ranging from 50 to 10^{-6} Pa. (4) Completion of the development of methods for the determination of Vitamin D_2 and lactose in powdered milk formulations in preparation for certifying these analytes in an SRM. (5) Development of a vidicon-based fluorescence detection system for qualitative and quantitative analysis of HPLC effluents. The performance of the system was evaluated by quantifying a number of PAH in an extract of SRM 1649, Urban Dust. (6) In collaboration with the Organic Electrochemistry Group, investigation of several approaches to the selective determination of nitro-PAH derivatives in complex mixtures. The most promising approach involves the isolation of a nitro-PAH fraction on a cyano-amino column, separation of individual nitro-PAH species by reversed-phase HPLC, on-line zinc catalytic reduction of nitro- to amino-PAH, and spectrofluorometric detection. (7) Development of sample preparation and HPLC procedures for the determination of PAH in mussels in conjunction with the Pilot National Environmental Specimen Bank program. (8) Extension of on-line multidimensional HPLC investigations to the analysis of amino- and nitro-substituted PAH compounds. Class separations were found possible and analytical separations among class members were achieved. We experienced problems with desorption of these compounds from our interface column and are currently investigating several possible solutions to this problem.

The group has actively participated in the NBS Standard Reference Material (SRM) program. During the past year, the LC Group was involved in the certification of the following SRM's: (1) SRM 1649, Urban Dust/Organics. An HPLC method involving gradient elution and fluorescence wavelength programming was one of the two analytical techniques used to measure 13 PAH in extracts of this material. This SRM is intended primarily for use in the evaluation and calibration of analytical methods for the determination of PAH on atmospheric particulate matter or on similar materials. (2) SRM 1599, Antiepilepsy Drugs in Human Serum. HPLC methods were used to determine the concentrations of valproic acid and carbamazepine in a lyophilized human serum material. This SRM will be used for calibration and standardization of procedures employed in clinical laboratories. (3) SRM 998, Angiotensin I. HPLC was used in the determination of the purity and total peptide content of this material. This material will be used as a reference material for radioimmunoassay of renin and can also be used as a peptide standard. (4) SRM 1639, Organics in Drinking Water. HPLC, using a photoconductivity detector, was one of the techniques used to verify the concentrations of seven halocarbons in this methanol solution. This SRM is intended for the preparation of aqueous solutions for quality assurance in the analysis of halocarbons in drinking water. (5) SRM 1595, Tripalmitin. HPLC was used to aid in the determination of the purity of this material. This SRM is intended to be used as a reference material for the determination of triglycerides in human serum.

SRM activities currently in progress include the certification of p-aminobenzoic acid in phenacetin (SRM for differential thermal gravimetric analysis), organics in petroleum crude, and indeno(1,2,3-cd)pyrene generator columns. Next year we anticipate certifying a diesel particulate extract for PAH and nitro-PAH content as well as certifying a phenols-in-hexane calibration solution SRM.

During the past year, Drs. Freeman Allen, Pomona College, Claremont, Ca., and Corazon Vogt, University of Missouri, Columbia, Mo., conducted sabbatical research in our Group. Dr. Allen was primarily involved with the development of sample preparation procedures for the determination of pesticides and PAH in human and animal tissues. Dr. Vogt investigated the feasibility of using reductive amperometry for 1) direct HPLC detection of nitro-substituted PAH, and 2) on-line reduction of non-fluorescent nitro-PAH to their highly fluorescent amino derivatives with subsequent fluorescence detection.

During the coming year we plan to continue our efforts in LC/MS and our studies in retention mechanisms. The latter should be bolstered by the arrival of Dr. Lane Sander, an NRC Postdoctoral Fellow from the University of Washington.

We plan to continue our efforts in multidimensional HPLC and expand our competence in pre- and post-column derivitization techniques. We will reduce slightly our efforts in the environmental area while expanding our efforts in the clinical and food analysis areas.

Willie E. May, Group Leader; Charles F. Allen, Jeanice M. Brown-Thomas, Richard G. Christensen, Walter F. Kline, Sam A. Margolis, William J. Sonnefeld, Corazon R. Vogt, Robert B. Weker, Stephen A. Wise

5. Mass Spectrometry Group: Overview

The Mass Spectrometry Group has devoted the major part of its efforts to the quantitation of individual compounds in complex mixtures, the development of high-resolution mass spectrometric techniques for the analysis of high molecular weight compounds, the continued development of a liquid chromatography/mass spectrometry (LC/MS) interface compatible with reversed-phase LC, and research, begun last year, which is part of a competence building program, "Analysis of Ionization Mechanisms and Ion Structures." Other agency and programmatic research continue to be concentrated in the environmental and clinical areas.

Development of isotope dilution definitive methods for the quantitation of human serum constituents has continued in collaboration with the Bioanalytical Techniques Group. A human serum Standard Reference Material, SRM 909, released in 1980 was previously certified for the concentrations of cholesterol, glucose, and uric acid. A method has been developed for urea and the collection of data for certification is complete. The results of a cooperative study with the Karolinska Institute comparing isotope dilution/mass spectrometry (ID/MS) methods for cholesterol has been published in Clinical Chemistry and a manuscript describing the two ID/MS methods developed for glucose will appear in Biomedical Mass Spectrometry in September. Methods are being developed for creatinine and triglycerides.

Further work, joint with the Liquid Chromatography Group, has been done on the LC/MS interface developed at NBS over the last several years. Development of a system which employs continuous sample preconcentration and ultrasonic nebulization for the introduction of aqueous mobile phases has been completed.

A method to obtain complete high-resolution field desorption spectra and accurate mass measurements using silver sulfonate salts for mass calibration with photoplate detection has been developed. Tests on a variety of peptides have given satisfactory results over the range of 300-1150 mass units. This work will comprise the Ph.D. thesis to be presented to The American University by a guest worker in our Division, Rafael Espinosa-Leniz.

Research has continued on development of isotopically labeled marker compound standards for use in the proposed Environmental Protection Agency (EPA) "Master Analytical Scheme" for priority pollutant analysis. Additional sets of internal standards have been prepared and delivered to EPA. These new standards consist of two or three concentration levels each of five different mixtures and contain a total of twenty deuterated compounds and one unlabeled compound. Work is in progress on confirming the chemical and isotopic stability of these solutions. Similar sets of labeled marker compound standards are being prepared for use by EPA and its contractors in a "Comprehensive Scheme for Soils, Sediments, and Sludge."

Research in the environmental area has focused mainly on the development of accurate quantitative methods for the determination of trace level organic compounds in aqueous wastes associated with energy production. High-resolution capillary column gas chromatography/mass spectrometry with selected ion monitoring has provided the selectivity and sensitivity necessary for quantitation of individual organic species in complex samples such as a shale oil process water and in aqueous leachates of hazardous wastes (Solvent Refined Coal II Vacuum Still Bottoms, H-Coal Filter Cake) at the part-per-billion (μg/L) level. Initial experiments have been carried out to develop both electron impact and methane chemical ionization GC/MS methods for the determination of individual organic compounds in a Wilmington crude oil. The methods will be used for a Wilmington Crude Oil SRM certification. Work has begun, in conjunction with the Gas and Particulate Science Division, on the development for EPA of standards for trace (ppb) toxic organic chemicals in air. The group continues to provide support for other environmental projects within the Division such as the qualitative identification of polynuclear aromatic hydrocarbon species in the Washington Urban Dust which has recently been issued as SRM 1649.

A competence building program in mass spectrometry, "Analysis of Ionization Mechanisms and Ion Structures," was begun in October 1980. One part of this program involves laser induced metastable ion generation as a selective probe for molecular structure. The photodissociation of ions created by electron impact was observed for a variety of molecules last year using borrowed equipment. This year permanent equipment--an argon ion laser, a chopper, optics, and a lock-in amplifier--has been installed, and the dependence of the photodissociation on wavelength observed in other laboratories has been confirmed. A second part of the program, the study of the collision of ions with reactive neutral species, was scheduled to begin this year. An existing quadrupole mass spectrometer has been modified by the manufacturer to the triple quadrupole required. During this year both of the principal investigators in the competence building program served on the NBS panel which reviewed the analysis for organic chemicals performed by EPA in its Love Canal Monitoring Study.

Research planned for the coming year includes: continuation of the ongoing environmental projects with particular attention to the use of alternative ionization techniques, such as chemical ionization and negative chemical ionization to obtain increased sensitivity and/or selectivity of detection for quantitation; development of isotope dilution definitive methods for creatinine and triglycerides, and implementation of improvements to the instrumentation used; and, for the competence building program, the study of the photodissociation of ions of low internal energy, such as field desorbed ions, as a potential source of structure information and the start of studies on the collision of ions with reactive neutral molecules.

Edward White V, Group Leader; Rafael Espinosa-Leniz, Laurence R. Hilpert, Stanley Meiselman, Kristy L. Richie, Lorna T. Sniegoski, Michael J. Welch, Corazon R. Vogt

6. Spectroscopy Group: Overview

During the past year, the Spectroscopy Group has energetically continued its programs in organic analysis by NMR spectroscopy, polarimetry, SRM certification, and the synthesis of isotopically labeled and unlabeled bioorganic materials. The Group has declined in number as the two NBS-NRC postdoctoral research associates have completed their appointments.

During the past year, substantial progress has been made with the analytical application of NMR spectroscopy. Proton NMR at high field has been used in two different ways to complete certification of the Angiotension I SRM; firstly, by measurement of acetate content, and secondly, for verification of amino acid composition.

Proton nuclear Overhauser effect difference techniques have been used at 400 MHz for proof of the identity of a commercial sample of 13-methylpicene needed for theoretical studies of liquid chromatographic retention times. This project involved comparative studies of the high field spectra of a group of related PAH.

Studies of the proton and ^{15}N NMR of neomycin B and its related aminoglycosides have now been completed. Our initial, intuitive analysis of the complex 400 MHz proton NMR spectrum of neomycin B has been confirmed by two-dimensional, J-resolved NMR techniques, thus verifying our previous ^{15}N results that the conformation of the L-idose moiety is different from that reported in the literature. A paper on the ^{15}N component of this work has been accepted for publication by the *Journal of the American Chemical Society*.

Our postdoctoral research project on the synthesis and analysis of intermediates leading to anti-tumor nucleosides and nucleotides has been pursued in several new directions. A new class of 2-methylthio-oxazoline derivatives of carbohydrates has been synthesized by methylation of 2-thiono oxazolidine derivatives. The ^{13}C and ^{15}N isotopically labeled modifications of the methylthio intermediates have been studied extensively by multinuclear NMR techniques with the objective of developing correlations of heteronuclear NMR parameters with structure.

In work designed to test the synthetic utility of carbohydrate oxazolines, a novel fructose diphosphate (FDP) analogue of cyclouridine has been synthesized by condensation of the 2-amino oxazoline derivative of FDP with methyl propynoate.

The previous syntheses of 2-amino oxazoline derivatives of monosaccharides have been extended to a variety of disaccharides and a trisaccharide, including examples in the cellobiose, lactose, maltose, palatinose, 3-O-α-D-glucosylarabinose, 3-O-β-D-galactosylarabinose, and maltotriose series. Studies of the ^{15}N NMR spectra of the ^{15}N labeled modifications have indicated a dependence of ^{15}N chemical shifts on the ring size of the sugar moiety.

A substantial upgrading of the capability of the WM-400 spectrometer has been accomplished this year by installation of an advanced pulse programmer. This installation required quite major revisions of the console hardware and of the computer software so that for 2-3 months, only partial operation of the spectrometer was possible. The new pulse programmer permits simultaneous pulses and phase control on the observe, decoupling, and receiver channels, thereby opening a new realm of multiple pulse, heteronuclear two-dimensional, and polarization transfer experiments. Work on certification of the Tripalmitin SRM has continued during the year, and the pulse programmer has allowed the first two-dimensional, J-resolved ^{13}C NMR spectra of tripalmitin to be obtained, in which the proton coupled, ^{13}C multiplets are displayed separately from the ^{13}C chemical shift information. Sensitivity enhancement by cross polarization (polarization transfer) methods is being implemented for ^{13}C and ^{15}N NMR. Instrumentation plans for the coming year include installation of a magnetic tape drive to facilitate archival mass data storage for both CP-200 and WM-400 NMR spectrometers, and also a computer switchable, ^{13}C/proton dual frequency preamplifier and probe (for the WM-400) that will allow the automated, sequential acquisition of proton and ^{13}C NMR spectra from 5-mm samples during overnight runs.

In polarimetric work designed to secure international agreement on a proposed change to the 100 °S calibration point of the sugar scale, the laser wavelength used for measurements of highly pure sugar solutions at NBS in 1978 has been verified by measurements of internationally standardized quartz rotators. Future plans in this area include the ongoing calibration service for quartz plates submitted by industry, and the use of the high accuracy polarimeter for recertification of the dextrose SRM, work in which high field proton and ^{13}C NMR are also expected to play an important role.

Bruce Coxon, Group Leader; Robert M. Davidson, Diane K. Hancock

B. Selected Technical Reports
(Organic Analytical Research Division)

1. The Effect of C_{18} Surface Coverage on Selectivity in Reversed-Phase HPLC (11320)

W. E. May, S. A. Wise

Several recent studies in the literature have reported selectivity differences for polycyclic aromatic hydrocarbons (PAH) on different octadecylsilane (C_{18}) liquid chromatographic column packing materials. The understanding of the origin of such selectivity differences would allow the chromatographer to "custom design" a column to optimize a particular separation. To investigate the origin of these selectivity differences, the C_{18} surface coverages (μmoles/m^2) of seven different C_{18} packing materials were determined from surface area measurements [Brunauer, Emmett, and Teller (BET) gas adsorption method] and percent carbon measurements on the chemically modified silica packing. Based on the C_{18} surface coverage data and manufacturers information, three of the C_{18} materials were determined to be "polymeric" phases and four were determined to be "monomeric" phases.

Some interesting trends were observed between retention on monomeric *vs.* polymeric C_{18} phases. For example, chrysene and benz[*a*]anthracene reverse elution order as the surface coverage increases and biaryl PAH (e.g., terphenyls, quaterphenyls, and phenyl-substituted PAH) are retained longer, relative to fused ring PAH, on monomeric than on polymeric C_{18} materials. Selectivity differences have been observed for PAH on different lots of C_{18} material from the same source. The effect of C_{18} surface coverage on PAH selectivity was investigated by examining six lots of 5 μm polymeric C_{18} packing material from one manufacturer. The physical characteristics (i.e., surface area and percent carbon) of these six lots are summarized in Table 14. As expected k', the capacity factor, for a test solute, benzo[*a*]pyrene (BaP), increases with increasing surface coverage. The selectivity differences (relative to BaP on five different polymeric C_{18} columns and a monomeric C_{18} column are illustrated in figures 23 and 24. The unusual behavior of biaryl PAH (figure 24) and other non-planar PAH such as phenanthro[*3*,*4*-*c*]phenanthrene (no. 5 in figure 23) and 1,2,3,4,5,6,7,8-tetrabenzonaphthalene (no. 6 in figure 23) indicate that solute planarity has a significant affect on PAH retention. Other structural features of the solute such as length-to-breadth ratio also affect the reversed-phase retention. In general, the selectivity factor (α) for PAH solutes with length-to-breadth ratios greater than 1.60 increase significantly with increasing carbon surface coverage (e.g., compound nos. 17-19 and 21-23 in figure 23), whereas α for solutes with smaller ratios tend to decrease with increasing surface coverage. Similar results have been observed for sulfur-containing PAH. The selectivity information in figures 23 and 24 can be used to select the appropriate column for optimization of a particular separation. Future studies will focus on determining the differences in the nature of the bonded surfaces for monomeric and polymeric phases which account for these selectivity changes.

Table 14. Physical Characteristics for Different Lots of Polymeric C_{18} Material[a].

Column	% C	Surface Area (m^2/g)[b]	Surface Coverage ($\mu mol/m^2$)	k'(BaP)[c]
1423S	4.5 ± 0.3[d]	48.5	4.3 ± 0.3[d]	2.7
1467	7.7 ± 0.6	61.0	5.8 ± 0.5	3.3
1460-12	7.7 ± 0.4	60.0	5.9 ± 0.3	3.5
1465	7.5 ± 0.5	61.6	5.6 ± 0.4	4.0
1703	8.0 ± 0.3	50.1	7.4 ± 0.3	5.0
1460-3	8.1 ± 0.3	48.3	7.8 ± 0.3	6.3

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[a] Vydac 201TP 5 μm materials.

[b] Determined by BET.

[c] 85% CH_3CN in H_2O.

[d] Uncertainty is ±1σ for three determinations.

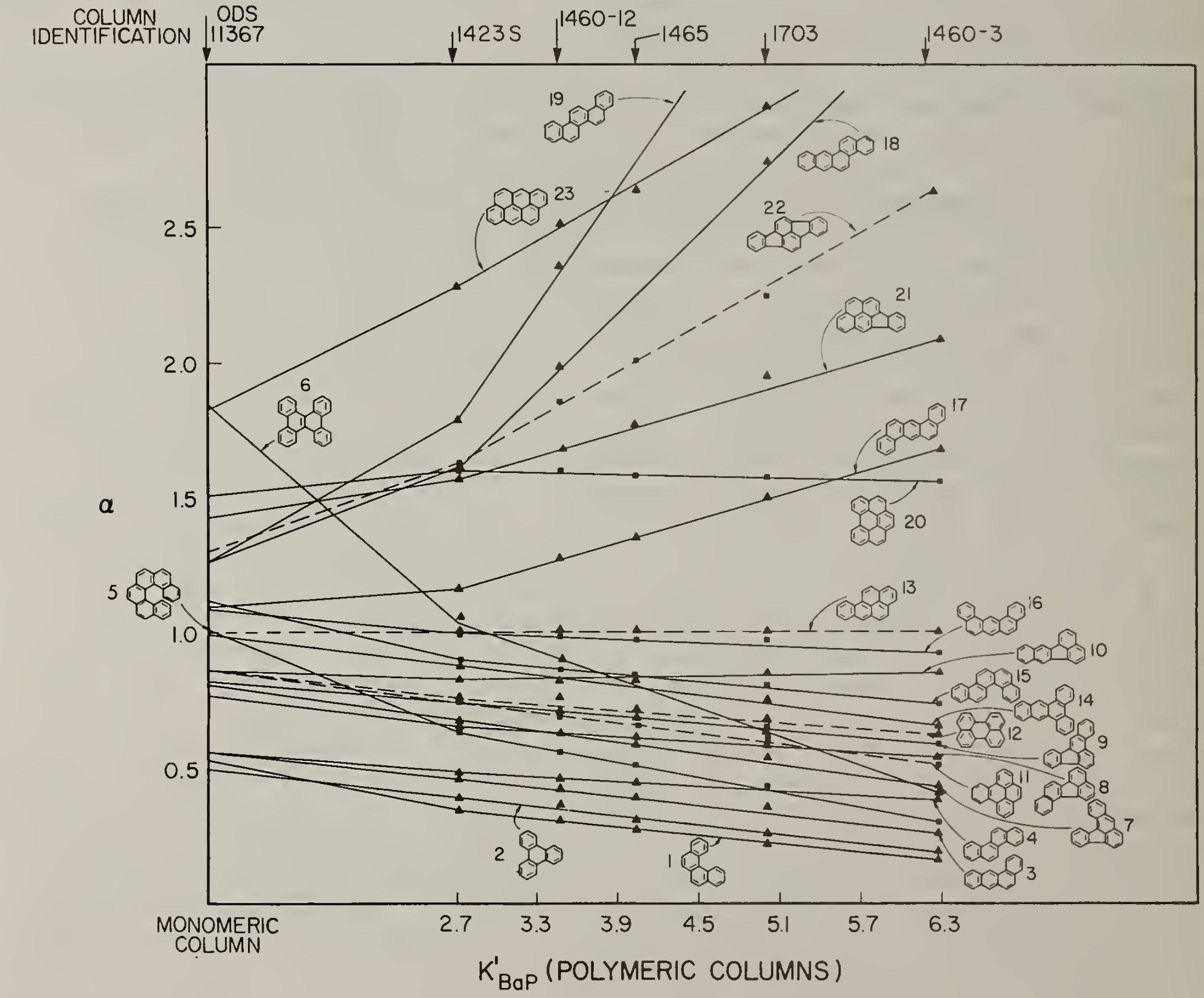

Figure 23. Selectivity factor (α), relative to benzo[a]pyrene, of selected polycyclic aromatic hydrocarbons on a monomeric C_{18} column and five polymeric C_{18} columns. (Polymeric columns arranged in order of increasing k' of benzo[a]pyrene.)

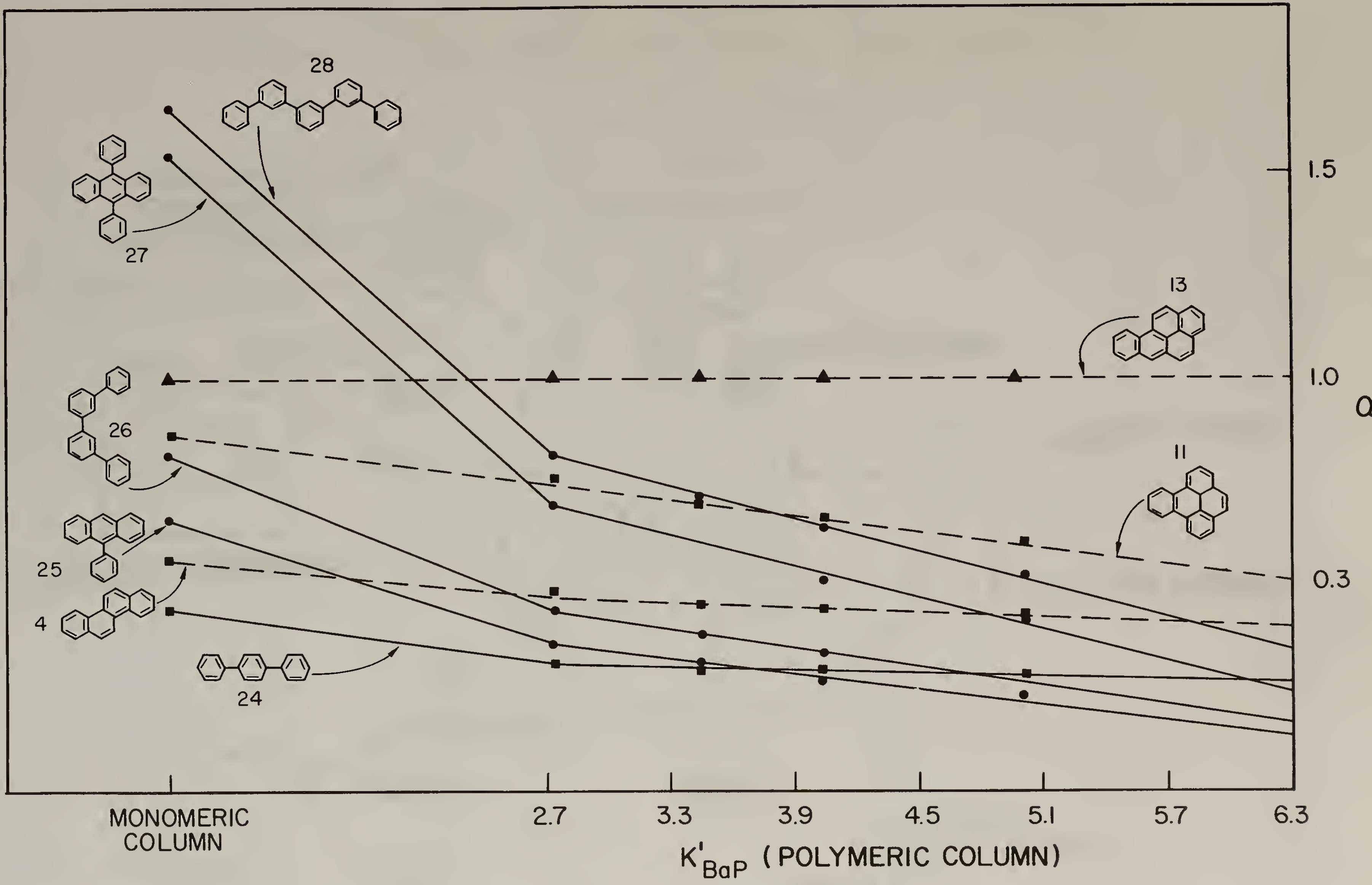

Figure 24. Selectivity factor (α), relative to benzo[a]pyrene, of selected biaryl PAH on a monomeric C_{18} column and five polymeric C_{18} columns. (Polymeric columns are arranged in order of increasing k' of benzo[a]pyrene.)

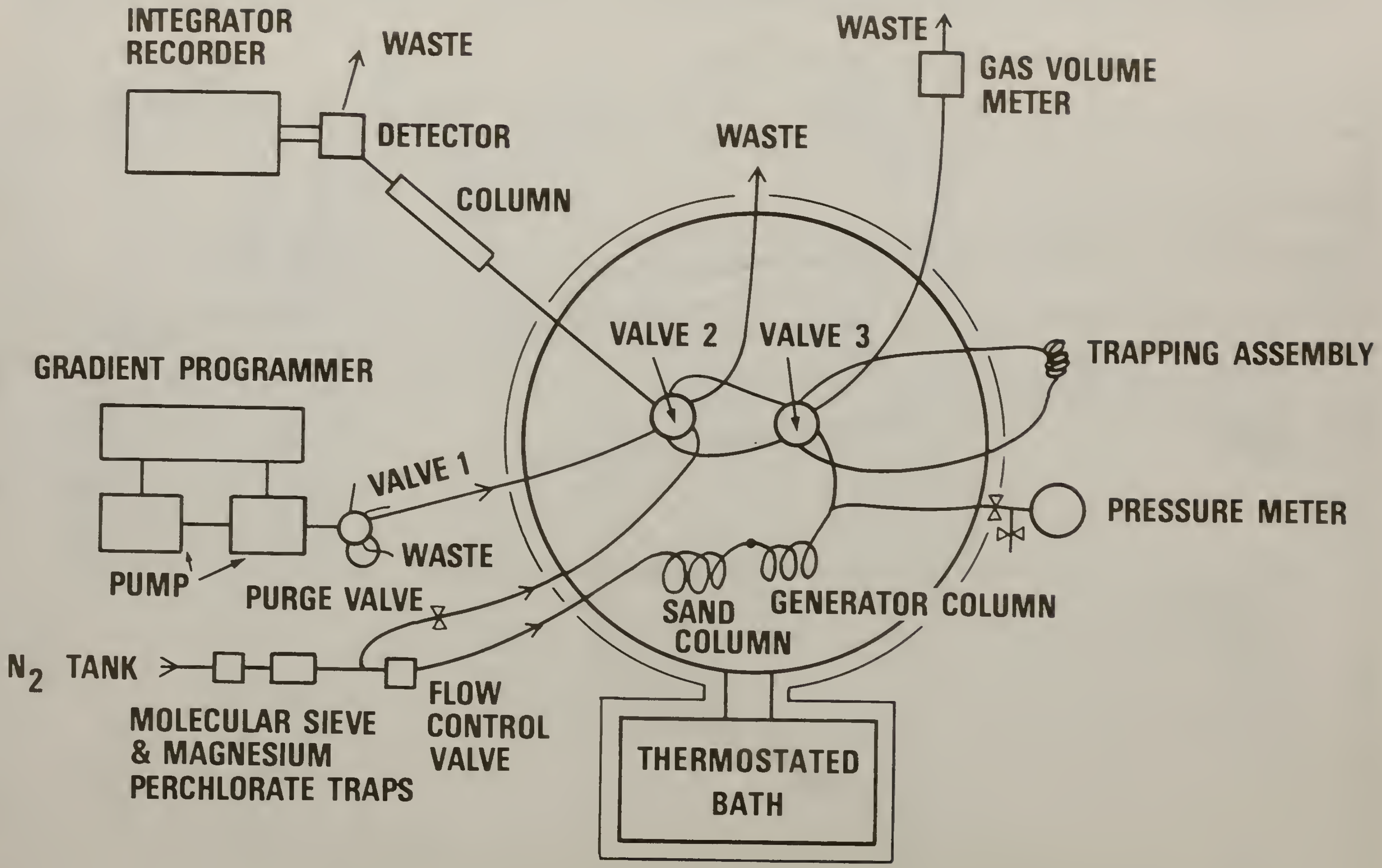

Figure 25. Coupled column HPLC/vapor generator column assembly.

2. Determination of Ambient Temperature Vapor Pressures of Polycyclic Aromatic Hydrocarbons (11320, 14230)

W. E. May, W. J. Sonnefeld

During the past decade, increased concern has developed about the environmental impact of anthropogenic trace organic compounds. One factor which governs the transport of organic compounds, both in the workplace and in the general environment, is the volatility of these compounds. The vapor pressure of a compound determines, in part, the rate of evaporation from industrial or waste sites, as well as the compound's tendency to be adsorbed by particulate matter present in the environment. Vapor pressure data can be combined with aqueous solubility data to calculate Henry's law constants, which can be used to predict the equilibria of dissolved organics in water with their atmospheric concentrations. The determination of the vapor pressures of organic compounds in the ambient temperature range (0-50 °C) is therefore important to permit the development of environmental transport models, as well as for the assessment of possible health hazards present in the atmosphere.

During the past few years, we have developed a gas-saturation method utilizing high performance liquid chromatography (HPLC) for analyte measurement. The HPLC is directly coupled to the vapor saturator (generator) column, thus avoiding the associated problems of subsampling and sorption/desorption efficiencies found in some of the earlier methods. Furthermore, the time for the determination is decreased, since small volumes are collected and the entire amount of analyte, not an aliquot, is ultimately measured.

The experimental system (figure 25) is composed of three sections: a generator column for the production of an analyte saturated vapor; an extraction section for the collection and concentration of the analyte vapor; and a reversed-phase HPLC system for the measurement of the collected material.

The generator column consists of a tube filled with either the pure analyte or with an inert support material on which the analyte has been coated. Two methods of collecting and concentrating the effluent from the generator column have been employed: a packed superficially porous octadecylsilane column and a cryogenic trap. Comparable results have been obtained with these two collection devices.

The vapor pressures of organic compounds for which adequate HPLC detectors are available can be measured over a vapor pressure range from 50 to 10^{-6} Pascals. The accuracy has been estimated to be better than 95 percent by a propagation of errors treatment, with an average precision less than 6 percent relative standard deviation. The method has been used to determine the vapor pressures of selected polynuclear aromatic hydrocarbons (PAH) in the temperature range of 283.15 to 323.15 K (Table 15). The determination time ranges from 15 minutes to 3 hours depending on the total volume sampled and the flow rate of the generator column. The results of the measurements of the vapor pressures are generally in good agreement with extrapolated results reported in the literature which were determined using different methods at higher temperatures (Table 16). The enthalpies of sublimation for the PAH were determined from the temperature dependence of the vapor pressures and compared to literature values, with agreements of better than 15 percent (Table 17).

Table 15. Values of Constants for Calculating Vapor Pressures (Pascals) of Polynuclear Aromatic Hydrocarbons Between 283.15 and 323.15 K.

Compound	$\log P° = -A/T + B$ A[a]	 B[a]
Naphthalene	3960.03 ± 58.9	14.299 ± 0.200
Acenaphthylene	3821.55 ± 23.7	12.768 ± 0.079
Acenaphthene	4535.39 ± 47.3	14.669 ± 0.159
Fluorene	4616.07 ± 30.2	14.385 ± 0.101
Phenanthrene	4962.77 ± 32.8	14.852 ± 0.109
Anthracene	4791.87 ± 50.3	12.977 ± 0.170
Fluoranthene	4415.56 ± 46.2	11.901 ± 0.155
Benz[a]anthracene	4246.51 ± 132.2	9.684 ± 0.431
Pyrene	4760.73 ± 26.2	12.748 ± 0.087
Naphthalene (D_8)	3689.52 ± 27.6	13.392 ± 0.09
Phenanthrene (D_{10})	4704.13 ± 31.5	14.060 ± 0.11

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[a] The uncertainty of the constants A and B are the standard deviations based on >15 measurements at a minimum of 4 different temperatures.

Table 16. Vapor Pressures of Polynuclear Aromatic Hydrocarbons at 25.0 °C.

Compound	PAH Vapor Pressure, Pa This Work	 Literature Values Extrapolated to 25 °C
Naphthalene	10.4 ± 0.2	10.8, 10.8, 12.3
Acenaphthylene	$(8.9 \pm 0.2) \times 10^{-1}$	
Acenaphthene	$(2.87 \pm 0.9) \times 10^{-1}$	3.7×10^{-1}, 3.8×10^{-1}
Fluorene	$(8.0 \pm 0.2) \times 10^{-2}$	8.8×10^{-2}, 12.7×10^{-2}
Phenanthrene	$(1.61 \pm 0.04) \times 10^{-2}$	2.27×10^{-2}, 1.87×10^{-2}
Anthracene	$(8.0 \pm 0.2) \times 10^{-4}$	8.3×10^{-4}, 4.9×10^{-4}, 10.4×10^{-4}, 8.6×10^{-4}, 11.1×10^{-4}
Fluoranthene	$(1.23 \pm 0.07) \times 10^{-3}$	
Pyrene	$(6.0 \pm 0.2) \times 10^{-4}$	8.8×10^{-4}, 2.7×10^{-4}
Benz[a]anthracene	$(2.8 \pm 0.1) \times 10^{-5}$	2.2×10^{-5}

Note: All values are interpolated or extrapolated from log vapor pressure vs. 1/T(K) relationships. The mean values are shown with the standard deviation calculated from the average of the relative standard deviations for triplicate measurements at each of 4 or more temperatures.

Table 17. Average Enthalpy of Sublimation of Polynuclear Aromatic Hydrocarbons in kJ/mol Over the Temperature Range 10-50 °C.

	ΔH°_s, kJ/mol	
Compound	This Work[a]	Literature Values[b]
Naphthalene	75.8 ± 1.1	72.4, 72.7, 83.5
Acenaphthylene	73.2 ± 0.5	
Acenaphthene	86.8 ± 0.9	84.7, 82.1
Fluorene	88.4 ± 0.6	82.1, 82.8
Phenanthrene	95.0 ± 0.6	86.6
Anthracene	91.8 ± 0.9	103.8, 97.5, 98.5 102.8, 92.0
Fluoranthene	84.6 ± 0.9	84.7
Pyrene	91.2 ± 0.5	94.1, 95.2, 80.1
Benz[a]anthracene	81.3 ± 2.5	105

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[a] The uncertainty is ±1 standard deviation of the slope determined by a least-squares treatment of the raw data.

[b] Values are the average enthalpy of sublimation over the experimental temperature range in each study.

3. Determination of Polycyclic Aromatic Hydrocarbons in Complex Mixtures Using HPLC with Mobile Phase and Fluorescence Wavelength Programming

(11320, 14306)

W. E. May, S. A. Wise

One of the most common problems associated with the analysis of polycyclic aromatic hydrocarbons (PAH) in complex mixtures is the identification and quantification of individual isomers. Quantitative information on individual isomers is important because biological (toxicological) properties of many PAH have been shown to be isomer specific.

Reversed-phase high performance liquid chromatography (HPLC) has become a powerful tool for the separation of individual parent PAH. Retention in reversed-phase HPLC increases with the degree of alkylation. Thus, a serious problem associated with the identification of PAH based only on chromatographic retention in reversed-phase HPLC is the co-elution of alkyl substituted homologs of smaller PAH. For example, some alkyl phenanthrenes and anthracenes elute in the region where pyrene and fluoranthene elute; alkyl pyrenes and fluoranthenes co-elute with benz[a]anthracene and chrysenes, etc. In the past we have circumvented this problem by initially fractionating complex mixtures into isomeric PAH families via chromatography on an aminosilane column with a non-polar mobile phase, i.e., hexane. Each family can then be individually analyzed in a reversed-phase system, free of interferences from alkylated species of lower aromatic carbon number.

An approach that we have employed during the past year involves the use of reversed-phase HPLC with mobile phase (gradient elution) and fluorescence wavelength programming. In this approach, resolution of PAH with respect to time is achieved chromatographically. The fluorescence excitation and emission wavelengths being monitored are also changed with respect to time, so that each PAH being measured is monitored at wavelengths that are optimized for its detection. Since individual PAH have characteristic fluorescence spectra, it is possible to accurately measure one PAH in the presence of another known co-eluting PAH by the proper choice of detection parameters which need not be excitation or emission wavelength maxima. In addition, the characteristic nature of these spectra can aid in identification. The selectivity achieved using this approach is shown by comparison in figure 26. The upper chromatogram is a UV trace of the analysis of an extract of SRM 1649, Urban Dust/Organics. Individual PAH are practically indistinquishable. The remaining four chromatograms represent the analysis of the same extract using fluorometric wavelength programming. The specific excitation and emission wavelength pairs used and the compound measured are identified in Table 18.

Table 18. Fluorescence Conditions for the LC Determination of Selected PAH in Atmospheric Particulate Matter.

	Wavelengths (nm) (see figure 26)		
	Excitation	Emission	PAH Quantified
λ_1	285	450	fluoranthene and 7-methylfluoranthene (I.S.)[a]
λ_2	400	440	perylene-d_{12} (I.S.) and perylene
λ_3	295	405	benzo[_k_]fluoranthene, benzo[_a_]pyrene, and benzo[_ghi_]perylene
λ_4	330	385	pyrene
λ_5	285	385	benz[_a_]anthracene, dibenz[_a_,_h_]anthracene, and benzo[_ghi_]perylene
λ_6	290	360	phenanthrene
λ_7	270	360	chrysene
λ_8	300	500	indeno[_1_,_2_,_3_-_cd_]pyrene

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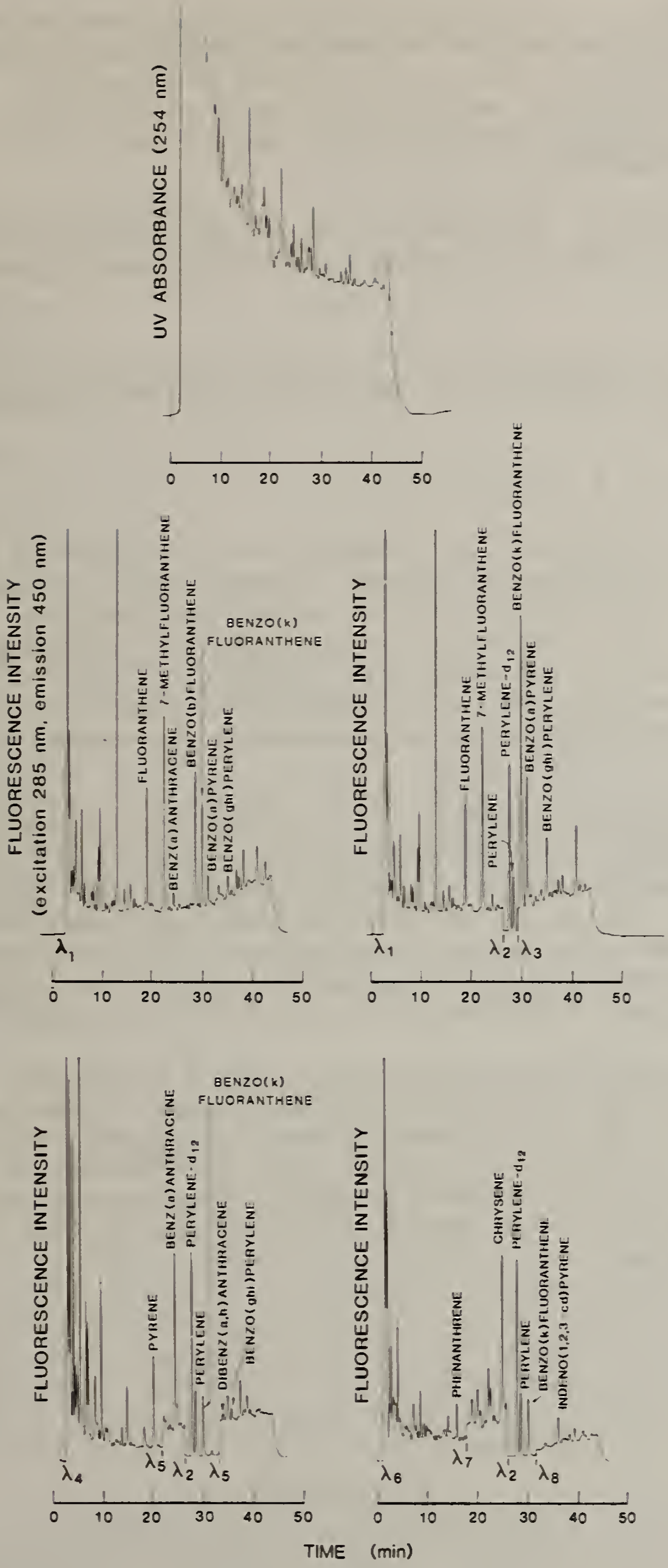
[a] I.S. - internal standard.



Excitation (λ)	Emission (λ)
λ_1 = 285	450
λ_2 = 400	440
λ_3 = 295	405
λ_4 = 330	385
λ_5 = 285	385
λ_6 = 290	360
λ_7 = 270	360
λ_8 = 300	500

Figure 26. Reversed-phase fluorescence wavelength programming method for analysis of raw particulate extract.

The hardware requirements for implementation of this technique are an HPLC pumping system capable of gradient elution and retention time reproducibility of ±6 seconds in a 45 minute gradient, and a spectrofluorometric detector capable of rapid scanning and excitation and emission wavelength programming. Wavelength accuracy and reproducibility needs to be ±2 and ±1 nm, respectively, with 10 nm slits.

This approach has been used in the certification of SRM 1649 and will be used to further measure PAH in extracts of mussels and diesel exhaust particulates.

4. Vidicon Based Fluorescence Detection for Qualitative and Quantitative Analyses in HPLC (11320)

T. H. Begley, W. E. May, R. A. Velapoldi

The increased interest in multiwavelength detection in HPLC has led to the development of vidicon based detection systems. These systems are capable of measuring the absorbance or emission spectra of the eluting compounds on-the-fly. In particular, vidicon systems used to measure the fluorescence of compounds offer high sensitivity and selectivity for HPLC. The use of HPLC-vidicon systems has not yet been applied for the routine analyses of complex samples where quantitative information about many components is desired.

We have successfully used an HPLC-vidicon system to determine quantitatively numerous polycyclic aromatic hydrocarbons in the NBS Urban Dust/Organics SRM 1649 (see Table 19). Summarized in the table are PAH concentration values determined by selective wavelength integration intervals (WII, column 1), signal-to-noise optimized WII (column 2), weighted HPLC averages from the SRM certificate (quadrature addition of ± values, one standard deviation of the mean, column 3), and the SRM certified values (column 4). Detection limits for these compounds have been determined and are in the 0.08-0.1 ng range.

A method to extract the qualitative spectrum of a weakly fluorescing component from a formidable background also has been developed. The method is based on a linear approximation of the background behavior. Studies included optimization of the wavelength integration interval (WII) with respect to signal-to-noise ratio, the use of the ratio technique to determine the purity of a chromatographic peak, and the use of second derivative spectroscopy to deconvolute co-eluting components.

Table 19. Analysis of NBS SRM 1649, Urban Dust/Organics

	Compound Concentration, μg/g					
	Selective WII[a]		SNR Optimum WII[a]		HPLC Avg.[b]	SRM[c]
Fluoranthene	7.1 ±0.8[d]	(35)[e]	7.5 ±1.2[d]	(251)[e]	7.0 ±0.5[d]	7.1±0.5
Benz[a]anthracene	2.1 ±0.5	(11)	2.1 ±0.2	(301)	2.7 ±0.3	2.6±0.3
Chrysene	4.0 ±0.6	(11)	9.0 ±3.0	(251)	3.6 ±0.2	
Benzo[b]fluoranthene	6.5 ±0.1	(35)	7.0 ±0.6	(301)	6.2 ±0.3	
Perylene	0.7 ±0.3	(11)	1.1 ±0.9	(179)	0.8 ±0.04	
Benzo[k]fluoranthene	2.2 ±0.3	(11)	2.7 ±0.6	(301)	2.0 ±0.1	
Benzo[a]pyrene	1.2 ±0.7	(11)			2.6 ±0.3	2.9±0.5
Benzo[ghi]perylene	3.5 ±0.2	(11)	4.1 ±0.3	(243)	4.5 ±0.7	4.5±1.1
Dibenz[a,h]anthracene	0.71±0.30	(11)	0.86±0.4	(221)	0.41±0.07	

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[a] WII = Wavelength Integration Interval.
SNR = Signal-to-Noise Ratios.

[b] Fluorescence with wavelength programming. See Technical Accomplishment #3 for further details on method. 7-Methylfluoranthene used as internal standard.

[c] Certified SRM values. The estimated uncertainties are intended to correspond to approximately 95% confidence limits. They represent an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material inhomogeneity.

[d] All ± values are one standard deviation of the mean.

[e] Numbers in parentheses are the width of WII in channels.

5. Certification of SRM 1649, Urban Dust/Organics, for Selected Polycyclic Aromatic Hydrocarbons (14306)

S. N. Chesler, W. F. Cuthrell, W. E. May, R. E. Rebbert, S. A. Wise

In recent years, many analysts have expressed interest in examining the organic content of SRM 1648, Urban Particulate Matter, which is certified only for its trace element content. As a result, NBS has issued a similar urban particulate material (collected in the Washington, D.C. area) which has been certified for several polycyclic aromatic hydrocarbons (PAH). SRM 1649, Urban Dust/Organics, is issued in 10 g quantities to provide ample material for a number of organic compound measurements.

As with the certification of other SRM's, two independent analytical procedures were used for the determination of selected PAH. Different sample extraction solvents, internal standards, and clean-up procedures were used prior to the separation and quantification by capillary column gas chromatography (GC) and high performance liquid chromatography (HPLC) as described previously (CAC Annual Report, 1981). The analytical results of these analyses are summarized in Table 20 for 14 PAH. The liquid chromatographic results are reported separately for the analyses using 7-methylfluoranthene and perylene-d_{12} as the internal standards (LC-I and LC-II in Table 20). Results using perylene-d_{12} as the internal standard were generally more precise than those determined using 7-methylfluoranthene. The certified values for 5 PAH are given in Table 21. The values for the remaining PAH (see Table 20) are provided to the user only as informational values since they were determined using only one method or sufficient agreement between the two methods was not achieved.

Table 20. Summary of Results by the Various Analytical Methods.

	Concentration, μg/g		
Compound	GC [4][a]	LC-I [18]	LC-II [9]
Phenanthrene	----	----	4.5 ±0.3[b] (9)[c]
*Fluoranthene	7.3 ±0.2[b] (4)	7.0 ±0.5[b] (24)	6.8 ±0.4 (9)
Pyrene	7.2 ±0.2 (4)	6.3 ±0.4 (17)	6.2 ±0.2 (9)
Chrysene	----	3.5 ±0.1 (5)	3.7 ±0.2 (9)
*Benz[a]anthracene	2.4 ±0.1 (4)	2.8 ±0.3 (18)	2.4 ±0.1 (3)
Triphenylene	----	----	1.7 ±0.1 (3)
Perylene	0.84±0.09 (4)	0.80±0.04 (17)	0.65±0.02 (9)
Benzo[e]pyrene	3.3 ±0.2 (4)	----	----
*Benzo[a]pyrene	3.0 ±0.3 (4)	2.6 ±0.4 (18)	2.6 ±0.1 (9)
Benzo[b]fluoranthene	----	6.2 ±0.3 (18)	----
Benzo[k]fluoranthene	----	2.0 ±0.1 (18)	2.1 ±0.1 (9)
*Benzo[ghi]perylene	4.7 ±0.2 (4)	3.9 ±0.8 (12)	5.2 ±0.6 (9)
Dibenz[a,h]anthracene	----	----	0.41±0.07 (9)
*Indeno[1,2,3-cd]pyrene	3.3 ±0.3 (4)	3.4 ±0.4 (16)	3.6 ±0.2 (9)

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[a] Number in [ ] indicates number of samples extracted.

[b] Uncertainty is one standard deviation of the mean.

[c] Number in ( ) indicates number of measurements.

*Indicates compounds with certified values in Table 21.

Note: LC-I used 7-methylfluoranthene as the internal standard and LC-II used perylene-d_{12} as the internal standard.

Table 21. Certified Values for Selected Polycyclic Aromatic Hydrocarbons.

Compound	Concentration, μg/g[a]
Fluoranthene	7.1 ± 0.5
Benz[a]anthracene	2.6 ± 0.3
Benzo[a]pyrene	2.9 ± 0.5
Benzo[ghi]perylene	4.5 ± 1.1
Indeno[1,2,3-cd]pyrene	3.3 ± 0.5

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[a] The certified value and the estimated uncertainty listed for a constituent are contained in the union of 95% confidence intervals computed separately for each analytical method and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material inhomogeneity. The estimated uncertainty is intended to correspond to approximately 95% confidence limits.

In addition to the quantitation of these major PAH constituents in SRM 1649, we have qualitatively characterized the complex PAH mixture extracted from the urban dust using multidimensional chromatographic techniques (i.e., LC-LC and LC-GC/MS). Over 40 unsubstituted PAH and sulfur-containing polycyclic aromatic compounds and numerous alkyl-substituted PAH have been identified from the Washington urban dust. Based on the current interest in the determination of PAH in air particulate samples, SRM 1649 should find widespread use in environmental analyses and serve as a useful benchmark sample for interlaboratory comparison of PAH determinations and for methods development.

6. Determination of Nitro-Polycyclic Aromatic Hydrocarbons Using Post-Column Reduction to Fluorescent Amino Derivatives (11320, 51101)

W. A. MacCrehan, W. E. May, W. J. Sonnefeld, C. R. Vogt

Nitro-polycyclic aromatic hydrocarbons (NPAH) are a class of compounds of recent and increasing environmental concern. 1-Nitropyrene and several dinitro-PAH have been shown to be among the most potent mutagens studied by the Ames assay. These compounds have been detected in gasoline and diesel engine emissions and in urban air particulate samples. Thus it is important to develop accurate measurement methods for NPAH.

Several avenues have been explored as possible means of selective and sensitive detection of NPAH in complex matrices. One simple approach is to use UV absorbance detection at a wavelength of 405 nm. Some of the other matrix constituents also absorb at this wavelength. We are presently using this approach in conjunction with other detection methods. However, this technique is not as sensitive or selective as we would like. We have also evaluated the use of reductive amperometric detection of the nitro group at a glassy carbon electrode. The hydrodynamic current-potential curves and the

LC detection limits have been measured for six NPAH. However, the use of this approach for gradient elution is quite cumbersome since oxygen must be rigorously excluded. The most promising approach for detection of NPAH appears to be chemical conversion to the amines, which may be detected by either fluorescence or oxidative amperometric detection.

The classical synthetic method for converting nitro compounds to their corresponding amines is reduction by metals in the presence of acid. We have adapted this approach with several constraints in mind. In order to achieve optimal performance for the liquid chromatographic separation, the compounds should be separated as the nitro derivatives, as the amines are often poorly behaved in the chromatographic system. The conversion must be done in an on-line fashion with little band broadening. It is important to achieve a high yield in the reduction to achieve reproducible results. In particular, the presence of unreduced NPAH must be minimized as these compounds have been shown to be fluorescence quenchers and could interfere with the detection of the amines formed. The pH of the solvent also has to be controlled as a compromise between sufficient acidity to favor the reduction:

$$R - NO_2 + 6H^+ + 3M^\circ \rightarrow RNH_2 + 2H_2O + 3M^{+2}$$

and yet not so acid as to protonate the arylamine product:

$$R - NH_2 + H^+ \rightarrow R - NH_3^+ \qquad pK_a \approx 4.7$$

since the $R - NH_3^+$ moiety is not fluoresent. Three pH values were tested: 5.0 and 5.8 (ammonium acetate/acetic acid) and 6.2 (ammonium succinate/succinic acid) using zinc as the reducing metal. The fluorescence signal was diminished about 15 percent at pH 5.0, with pH 5.8 and 6.2 giving equivalent signals.

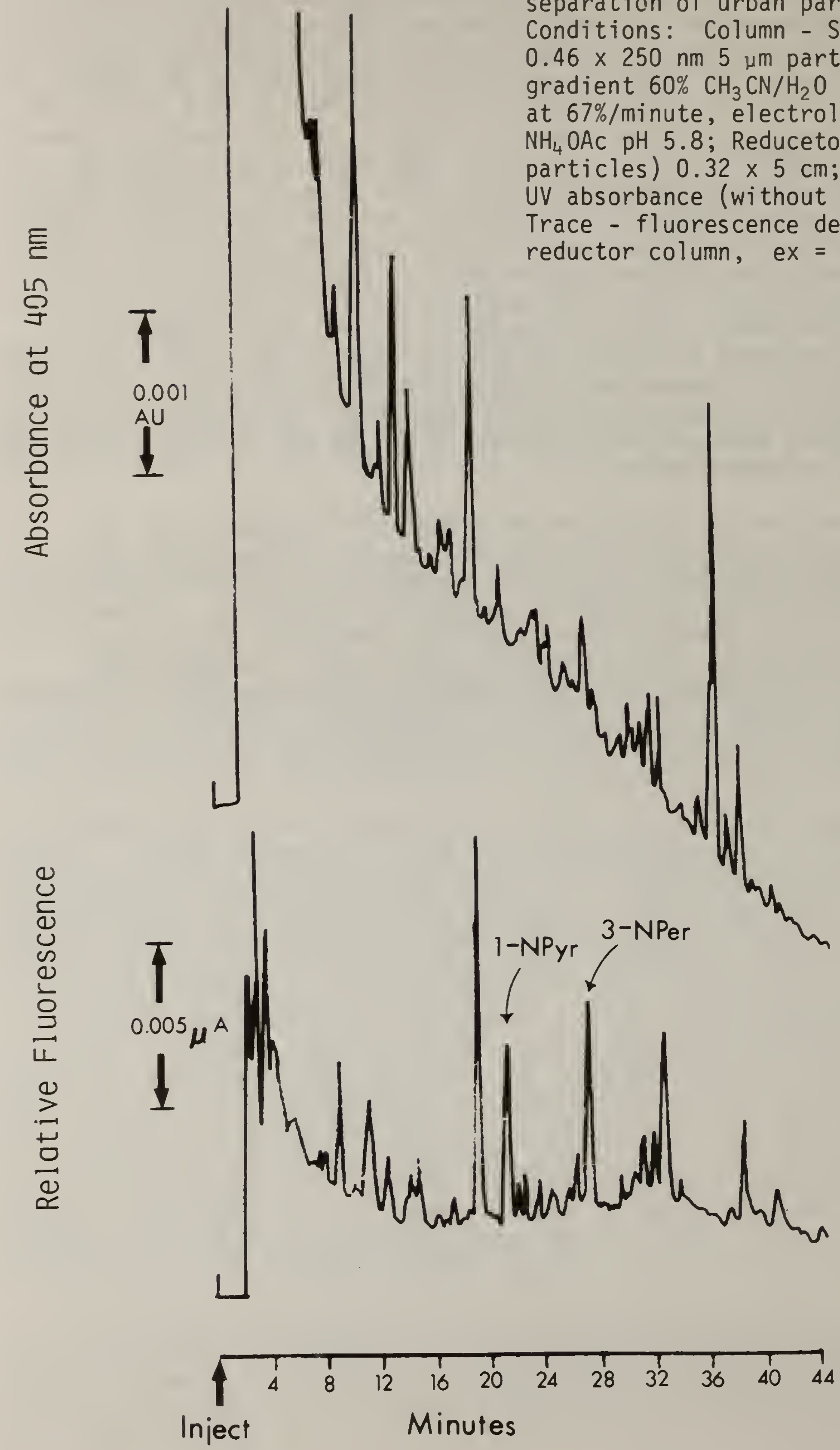
Several metals were compared for their efficiency of reduction of NPAH to amines. A small column (5 x 0.32 cm) was dry packed with fine particles (200 to 320 mesh) of each metal to be evaluated. This column was inserted after the column and UV detector of the LC but in front of the fluorescence detector. Using a 0.025 mol/L ammonium acetate buffer and a 1.0 mL/min flow rate, the conversion efficiency was determined for 1-nitropyrene and 1-nitronapthalene. Fairly large amounts of the test compounds were injected and the total volume for the peak eluting from the column through the fluorescence detector was collected. A sample of this fraction was reinjected and monitored with the UV detector. Two peaks were found for the "reduced" eluates: the expected amine and a trace of the unreacted nitro compound. By comparison to an appropriate standard, the conversion efficiency was evaluated. Zinc was found to give efficiences of 97-100 percent whereas cadmium gave only 55 percent. Aluminum, aluminum amalgamated with mercury, and magnesium were also evaluated but produced tiny bubbles in the eluent stream (probably from the reduction of hydrogen ion to hydrogen gas) and were thus unsuitable from a mechanical standpoint for use in the reductor column.

The effect of the concentration of electrolyte was also studied using zinc as the reductor packing. No conversion of the NPAH occurred when no electrolyte was used. As little as 0.001 mol/L of electrolyte caused substantial conversion, but the highest efficiency was found for a concentration of 0.1 mol/L buffer.

A gradient elution chromatographic separation was developed for NPAH using the following compounds: 1-nitronapthalene, 2-nitrofluorene, 9-nitroanthracene, 2-nitronapthalene, 1-nitropyrene, and 3-nitroperylene. The gradient program changed at 5 percent/minute from 60 percent CH_3CN (0.025 mol/L NH_4OAc pH 5.8) to 90 percent CH_3CN (0.025 mol/L NH_4OAc pH 5.8) at a 40 percent nonlinear rate. A chromatogram of an extract of the Washington Urban Particulate Matter SRM is shown in figure 27. The upper trace is the 405 nm absorbance of the unchanged compounds and the lower trace is fluorescence monitoring at 400 nm excitation (450 nm emission cut-off filter) after reduction in the zinc column. Only two peaks matched the retention time of our standards: 1-nitropyrene (1-NPyr) and 3-nitroperylene (3-NPer). Since this is a direct extract with no prior fractionation, many of the peaks may be compounds other than NPAH. In particular, quinones and simple polycyclic aromatic hydrocarbons have been found in similar samples and would be detected under these conditions. Current work involves fractionating diesel and air particulate extracts to separate extraneous compounds from the nitro compounds. We are also acquiring some quinones and dinitro-PAH to try to identify some of the unknown peaks in these samples.

We are actively trying to acquire additional NPAH compounds and are measuring the fluorescence spectra and electrochemical current-potential curves of the reduced compounds. This will allow us to choose the optimum conditions for fluorescence or oxidative amperometric detection. Of particular interest are the dinitro-PAH since they also have been found to be highly mutagenic. They are present in much smaller amounts than the mononitro compounds and will thus present more of a challenge for detector selectivity and sensitivity.

Figure 27. Gradient elution liquid chromatographic separation of urban particulate extract. Conditions: Column - Supelcosil C-18, 0.46 x 250 nm 5 μm particles, solvent gradient 60% CH_3CN/H_2O to 90% CH_3CN/H_2O at 67%/minute, electrolyte 0.025 mol/L NH_4OAc pH 5.8; Reducetor - Zn (200 mesh particles) 0.32 x 5 cm; Upper Trace - UV absorbance (without Zn reducer); Lower Trace - fluorescence detection following reductor column, ex = 400 nm.



7. Methods for the Determination of Vitamins in Milk (14301)

J. M. Brown-Thomas, S. A. Margolis, L. Watts, R. B. Weker

The primary objective of this program is to develop new methods and to apply established methods for the accurate measurement of organic nutrients, including vitamins, in food materials. Specifically, we expect to initially provide reference or certified values for organic nutrients in a proposed nonfat, dry milk SRM. During FY 81 we examined methods for the measurement of Vitamin D, lactose, and nicotinic acid. During the past year, we have improved the extraction methods for nicotinic acid and completed our work on Vitamin D and lactose. During FY 83 we anticipate completing our SRM measurements on nicotinic acid and beginning work on thiamin, lactic acid, and pyridoxine.

The accepted methods for the extraction of nicotinic acid from food matrices, such as autoclaving in strong acid or base, are harsh and lead to the formation of many undesirable products. Therefore, we have developed a milder extraction procedure using sulfosalacylic acid (SSA) as a protein precipitant in the presence of hydrochloric acid. This procedure allows the quantitative extraction of added nicotinic acid from milk samples. However, the use of this extraction method requires the modification of the analytical procedure to remove the highly UV-absorbing SSA before nicotinic acid analysis. This was achieved by using multidimensional chromatographic analysis. The sample was applied to an octadecylsilane (ODS) reversed-phase column which preferentially retained the SSA. The nicotinic acid was subsequently adsorbed onto an aminosilane column (connected in series to the ODS column) and eluted with a phosphate buffer gradient. This method allows the quantitation of nicotinic acid in milk samples which have been supplemented with 62 μg of nicotinic acid per gram of milk powder (containing 10 μg of native nicotinic acid by microbiological assay). The research to complete development of this assay procedure will include the refinement of the chromatographic process and development of a process for weak basic hydrolysis of the covalently bonded nicotinamide and its conversion to nicotinic acid.

The method developed for the analysis of Vitamin D involved the use of enzymatic (lipase) hydrolysis, HPLC separation of Vitamins D_2 and D_3 from the milk matrix with Vitamin D_3 as the internal standard, and a sequential HPLC procedure for final separation and quantitation. The lipase hydroyzate was fractionated on a cyanopropylsilane (CN) column using a 2 percent isopropyl alcohol/hexane mobile phase. Fractionation of a milk extract on a CN column is illustrated in figure 28. The lipase hydrolyzate fraction is between the dashed lines. Vitamin D_2 was separated from Vitamin D_3 and other co-extracted components by chromatography of the Vitamin D containing fraction on an acetonitrile mobile phase (figure 29). The D vitamins were measured by UV detection at 267 nm. The results of the analysis of Vitamin D_2 in a commercial milk formulation and in the SRM candidate dry milk material are summarized in Table 22.

The lactose content of the SRM candidate dry milk material was measured by HPLC utilizing a carbohydrate column. The lactose was eluted with 80 percent acetonitrile/water and measured with a refraction index detector (figure 30). By use of an external standard, the lactose content was found to be 44±1 percent (g/g) in the candidate SRM and 34±1 percent (g/g) in a commercial milk sample.

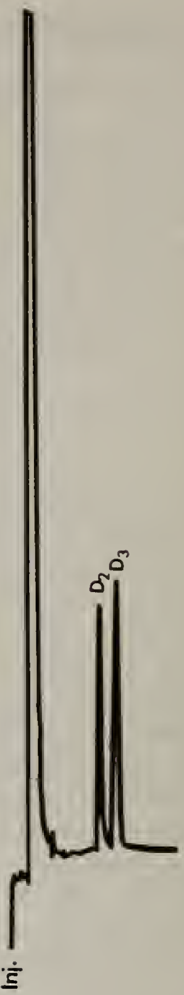


Figure 29. Analysis of a milk fraction for Vitamin D_2 on a reversed-phase column.

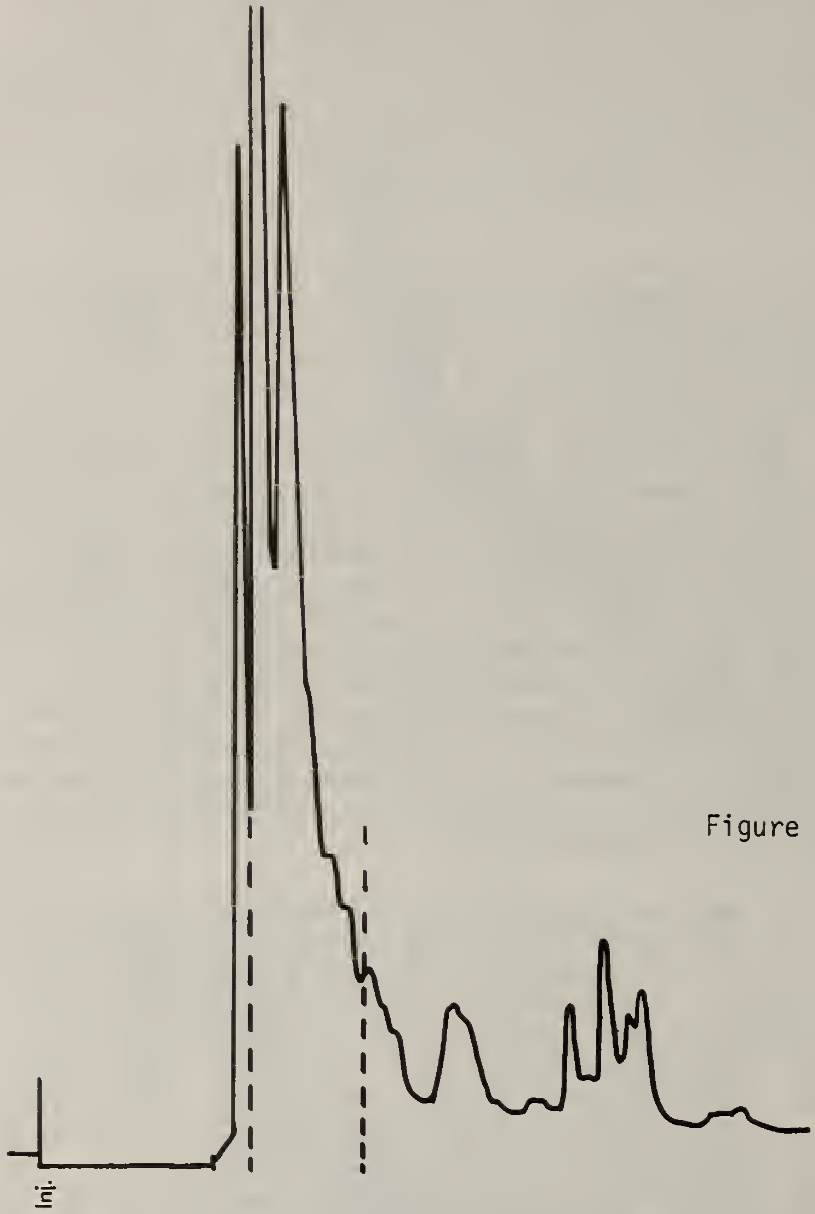


Figure 28. Fractionation of a milk extract on a CN column.

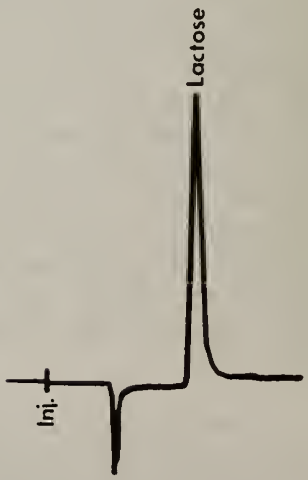


Figure 30. Analysis of lactose in a milk sample on a reversed-phase column.

Table 22. Concentration of Vitamin D_2 in Dry Milk.

Sample	D_2 (ng/g milk ± SD)
Commercial Fortified Material-Box 1	83 ± 3[a]
Commercial Fortified Material-Box 2	70 ± 3
Commercial Fortified Material-Box 3	95
Unfortified SRM candidate	<10

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[a] ± values represent standard deviation of a single measurement.

8. Certification of an SRM for the Anticonvulsant Drugs Carbamazepine and Valproic Acid in Serum (14306)

D. P. Enagonio, W. F. Kline, W. E. May, D. J. Reeder

In 1978, the NBS Office of Standard Reference Materials (OSRM) issued Standard Reference Material 900, Antiepilepsy Drug Level Assay Standard. SRM 900 contained four anticonvulsant drugs, phenytoin, ethosuximide, phenobarbital, and primidone. Since 1978, two additional drugs, valproic acid and carbamazepine, have become significant in the treatment of epilepsy. Consequently, a need exists for a Standard Reference Material containing these drugs. This year, the NBS OSRM will issue SRM 1599, which will contain valproic acid and carbamazepine at three concentration levels in freeze-dried human serum. Two independent analytical procedures were developed and used to certify the concentration levels of each drug in SRM 1599.

Determination of the drug levels by high performance liquid chromatography (HPLC) required a separate analytical procedure for each drug. Valproic acid was determined by a pre-column derivatization procedure in which valproic acid and an internal standard (cyclohexane carboxylic acid) were converted to their respective phenacyl esters after extraction from the serum matrix. The derivatized species were then measured by HPLC with UV absorbance detection at 254 nm. The concentration of valproic acid in the samples was determined from the area ratio of the derivatized valproic acid and internal standard versus the concentration of valproic acid in working standards.

The concentration levels of carbamazepine were determined by direct injection of reconstituted serum onto an HPLC reversed-phase column with 285 nm UV detection. Quantitation was accomplished by using bracketing external standards prepared in blank serum with concentrations around the target values of each SRM concentration level. We found it necessary to prepare external standard solutions in the blank serum rather than in an organic solvent, to correct for binding of carbamazepine to serum protein.

For the gas chromatographic (GC) analyses, known amounts of suitable internal standard compounds (cyclohexane carboxylic acid for valproic acid and cyheptamide for carbamazepine) were added to samples of the SRM, prior to extraction and analysis. The drugs and internal standards were extracted from the reconstituted SRM with chloroform. The chloroform layer was removed and concentrated to 50-200 μL. Multiple injections of these concentrates were made into the gas chromatograph.

The peak area ratio of drug to internal standard was compared with that similarly obtained from calibration samples. The calibration samples were prepared from blank serum to which known amounts of drug and internal standard were added. For each measurement, two calibration samples were used; one in which the concentration of drug and internal standard was 5 percent greater than the nominal concentration of drug in the SRM sample, and the other in which it was 5 percent less.

Tables 23 and 24 summarize the results obtained from each of the two independent procedures used in the certification of this SRM. Data reflecting the matrix effect associated with the HPLC determination of carbamazepine are given in Table 24. The certified concentration levels given in Table 25 are weighted averages of the results obtained from the GC and HPLC methods. The range gives an indication of the uncertainty of the certified value.

Table 23. Summary of Results Obtained from Analysis of SRM 1599 for Valproic Acid.

Concentration Level	Target Conc. (μg/mL)	Measured Conc., μg/mL HPLC	GC
High	145	144.5 ± .89[a]	140.4 ± .78[a]
Medium	65	67.0 ± .93	71.2 ± .42
Low	15	14.6 ± .25	14.3 ± .08

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[a] Uncertainties are expressed as the standard deviation of the mean concentrations.

Table 24. Summary of Results Obtained from Analysis of SRM 1599 for Carbamazepine.

Concentration Level	Target Conc. (μg/mL)	Measured Conc., μg/mL HPLC[a]	HPLC[b]	GC
High	19.9	17.5 ± 0.30[c]	19.9 ± 0.27[c]	18.9 ± 0.05[c]
Medium	9.4	8.20 ± 0.31	8.94 ± 0.04	8.60 ± 0.06
Low	3.0	2.60 ± 0.2	2.60 ± 0.03	3.0 ± 0.13

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[a] Ignores matrix effect, external standard made up in acetonitrile/water.

[b] Corrects for matrix effect, external standard prepared in serum base.

[c] Uncertainties are expressed as the standard deviation of the mean concentrations.

Table 25. Certified Concentrations for SRM 1599 (μg/mL)

	Valproic Acid			Carbamazepine		
	Low Level	Medium Level	High Level	Low Level	Medium Level	High Level
Concentration level	14.5	69.1	142.5	2.8	8.8	19.4
Range of results between methods	0.3	4.2	4.1	0.4	0.3	0.9

9. Research Results on the Analysis of Polychlorinated Biphenyls in Oils (14660, 14306)

S. N. Chesler, F. R. Guenther, R. M. Parris, R. E. Rebbert

The hybrid technique developed in our laboratory that utilizes both high performance preparative scale liquid chromatography and capillary column gas chromatography for the determination of polychlorinated biphenyls (PCB's) in hydrocarbon matrices has been used in the certification of a Standard Reference Material (SRM 1581) and for the analysis of 11 PCB-in-Oil NBS/ASTM round robin samples.

SRM 1581, Polychlorinated Biphenyls in Oil, consists of separate solutions of Aroclor 1242 and Aroclor 1260, each in a transformer oil and a motor oil base. Certified concentrations are listed in Table 26. This SRM is designed to be used as an external standard for analytical calibrations as well as a benchmark for interlaboratory comparisons. This SRM will be especially useful to the electrical industry where PCB contamination of transformer cooling fluid is of present concern, and in the motor oil recycling (re-refining) industry where inadvertent contamination of the recycling stock by PCB-containing fluids is a problem.

Table 26. SRM 1581, Polychlorinated Biphenyls in Oils, Certified Concentrations of Aroclor 1242 and Aroclor 1260 in Motor and Transformer Oils.

Matrix	Aroclor Type	Concentration, μg/g[a]
Motor Oil	1242	100 ± 1
Motor Oil	1260	100 ± 2
Transformer Oil	1242	100 ± 1
Transformer Oil	1260	100 ± 3

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[a] Uncertainty is expressed at the 95% confidence level.

In order to evaluate currently-used methods for the determination of Aroclors in oil matrices, a collaborative study was conducted by us, the NBS Recycled Oil Program, and the American Society for Testing and Materials (ASTM Committee D-2). Sets containing 11 oil samples representative of a range of PCB contamination in terms of Aroclor type and concentration were prepared and distributed to 19 laboratories. The oil matrices ranged from a virgin motor oil base to a used lubricating oil that had been collected for recycling purposes. All samples were gravimetrically prepared by us, except samples D and H which were used as supplied by the Office of Recycled Materials. Table 27 lists descriptions of the round robin samples and the results of our analyses as one of the participating laboratories. A chromatogram of sample J (see Table 27) is shown in figure 31. Quantitative data obtained and descriptions of the analytical technique used by each laboratory have been compiled and are being evaluated to identify accurate and efficient methods for the analysis of oils for PCB contamination.

Table 27. NBS/ASTM Round Robin Samples.

Code	Sample	NBS Results, μg/g[a]
A	5.9 ppm[b] Aroclor 1260/BC7345 oil	6.2 ± 0.3 Aroclor 1260
B,F[c]	41.0 ppm[b] Aroclor 1242/BC7345 oil	41 ± 1 Aroclor 1242
C	148.3 ppm[b] Aroclor 1260/BC7345 oil	147 ± 4 Aroclor 1260
D	BC7345 motor oil	Not Detected[d]
E,G[c]	41.0 ppm[b] Aroclor 1242 and 19.9 ppm[b] Aroclor 1260/BC7345 oil	41 ± 1 Aroclor 1242 19.8 ± 0.6 Aroclor 1260
H	BC7227 oil	165 ± 10 Aroclor 1260
I	96.6 ppm[b] Aroclor 1254/used oil 5482	80 ± 7 Aroclor 1254
J	1:9[b] #81-355-H oil/used oil 5379	25.4 ± 0.7 Aroclor 1242 48 ± 5 Aroclor 1254 40 ± 3 Aroclor 1260
K	1:4[b] Motor Oil Additive (CR-82R 5005)/ BC7425 oil	No recognizable PCB pattern

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[a] One LC fractionation, three GC runs; uncertainty expressed as 1 std. dev.

[b] wt/wt.

[c] Duplicate samples.

[d] Detection limit of <1 ppm Aroclor.

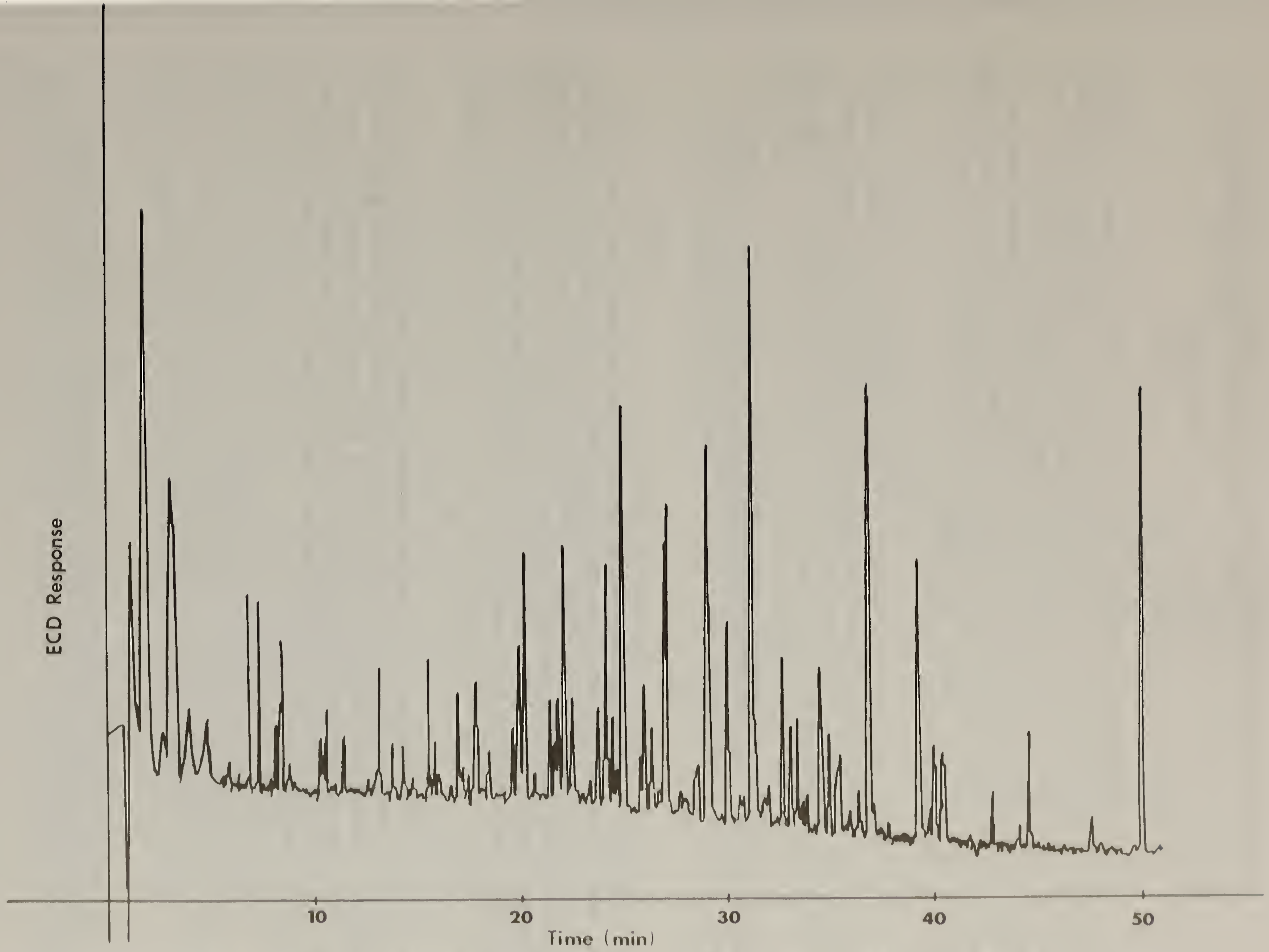

Figure 31. Gas chromatogram of HPLC fraction of NBS/ASTM round robin sample "J".

10. Analysis of a California State Reference Material for Pesticides in Sediment (14625)

S. N. Chesler, W. F. Kline

We have completed an analysis of a California State Department of Health Services (CSDHS) "Pesticides on Soil" test material. This material was prepared by CSDHS and consists of a soil spiked with six chlorinated pesticides at the µg/g level. This material will be used by CSDHS for proficiency testing of laboratories participating in a CSDHS study of hazardous waste analytical methodology. NBS was asked to analyze this material because CSDHS wanted confirmation of its own analysis prior to releasing this material for proficiency testing. NBS participated to satisfy CSDHS concerns as well as to gain experience in this analytical area.

The CSDHS test soil consisted of a finely divided dry sediment. Three 5.00 g soil samples were Soxhlet extracted with 300 mL of a 1:1 mixture of hexane and acetone. Prior to extraction, 3 mL of aqueous 0.2 mol/L NH_4Cl were added to the sediment to assure sample wetting during extraction. In addition, 9.74 µg of pentachlorobenzene and 10.38 µg of 2,2',4,4',5,5'-hexachlorobiphenyl in 1 mL of hexane were added to each unextracted sample to serve as internal standards (IS). Two solutions containing known amounts of each analyte and each internal standard were also Soxhlet extracted for determination of analysis response factors.

All samples were Soxhlet extracted for 18 hours and the extracts were analyzed by gas chromatography (GC) with electron capture detection. The GC was equipped with an immobilized phase wall-coated fused silica open tubular column. Duplicate analyses of the calibration solutions were used to determine gram response factors which were subsequently employed in the internal standard calculations for the sediment extracts. Independent calculations of the six analyte concentrations were made using each of the two IS compounds. The three sample extracts were analyzed at least in triplicate, and the results are exhibited in Table 28 along with the results obtained by CSDHS.

The results listed in the table are sufficiently encouraging that we are planning to propose that a pesticides on soil Standard Reference Material (SRM) be funded for issuance in FY 84. This SRM could be used as a primary standard for calibration of such complex analyses, and as a primary standard against which proficiency testing samples such as the one being released by the CSDHS could be evaluated.

Table 28. Results of Analyses of Pesticide Test Material.

	Spiked Level µg/g	NBS[a]			CSDHS		
		Mean	S.D.[b]	% S.D.	Mean	S.D.	% S.D.
Lindane	8	7.63	.16	2	7.68	.48	6
Heptachlor	6	4.08	.10	2	4.65	.51	11
Aldrin	3	3.08	.10	3	2.91	.22	8
Heptachlor Epoxide	8	7.37	.17	2	7.32	.59	8
Dieldrin	---[c]	1.64	.04	2	1.44	.19	13
p,p'-DDT	4	4.01	.18	4	3.76	.31	8

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[a] Based on analyses of replicate samples.

[b] Standard deviation of the mean (1σ).

[c] Natural contaminant in the soil.

11. Design and Construction of a Sampling System for Woodburning Stove Gases and Particulate Samples (25005)

F. R. Guenther

To assess the relative contribution of woodburning stove emissions to respirable atmospheric particulate matter, profiles of gas and particulate discharge must be examined. Although both organics and inorganics can be utilized in this profile, the carcinogenic and mutagenic properties of some organics increase the importance of the organic contribution. During the past year, a preliminary study of the organic emissions from a wood stove has been completed.

In this preliminary study, collection and analysis of the phenolic fraction from the wood stove stack emissions has been emphasized. The sampling system consisted of a Pyrex gas sampling tube inserted through the walls of the stack into the center of the flow stream. The emission gases were drawn through this tube and through a porous polymer XAD-2 trap. The organics contained on the trap were removed by extraction with methylene chloride. The extraction was done immediately after sample collection. An internal standard was added to the extract after extraction, the sample was evaporatively concentrated and injected onto a semipreparative aminosilane liquid chromatographic column, and the fraction of the eluent containing the phenols was collected. This fraction was then evaporatively reconcentrated and analyzed by gas chromatography with a low-bleed, medium-polarity capillary column (DX-2).

Condensable organics were collected on a fine mesh screen inserted into the stack below each gas sampling port. These screens were extracted with methylene chloride in a sonic bath and analyzed by the same procedure outlined above.

Collection positions were located at the bottom and top of the stove stack. The wood stove utilized in these experiments was equipped with a baffle electronically controlled to limit stack temperatures to within 10 °C of a preset value. Collections were made at stack temperatures of 80-90 °C, 110-120 °C, and 140-150 °C.

The preliminary findings showed that 1) the relative amounts of individual phenolic species from this wood stove were essentially constant at the temperatures examined, 2) approximately 5-13 percent of the phenols present in the gas stream at the bottom of the stack was removed to the stack walls before reaching the top collection port, 3) phenolic production in the wood stove is inversely proportional to stack temperatures.

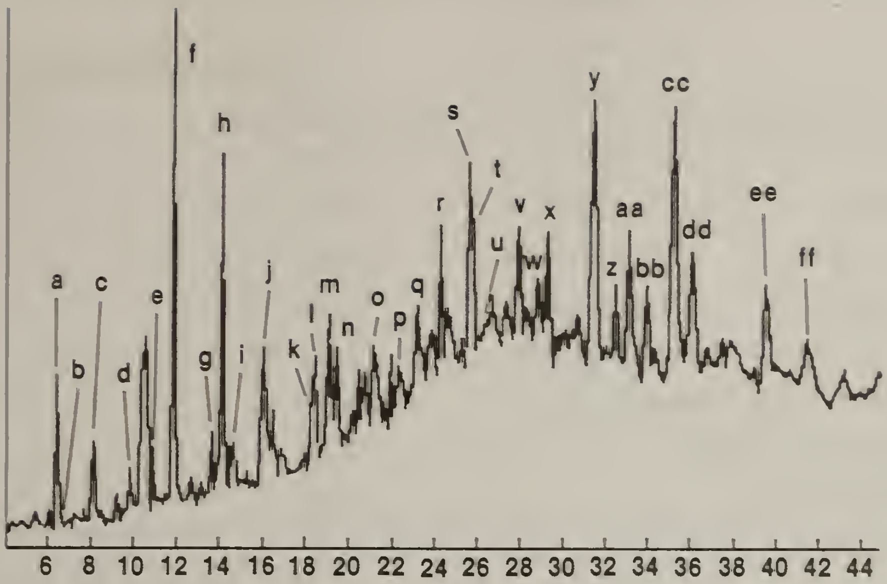
Plans for next year include: 1) redesigning the collection system, such that inorganics can also be determined (inorganic analyses will be done under the direction of Dr. William Zoller at the University of Maryland);
2) analyzing other compound classes such as polycyclic aromatic hydrocarbons, nitrogen-containing polycyclic aromatic compounds, ketones, and aldehydes;
3) collection from residential fireplaces and stoves; and 4) collection from newly designed wood stoves, such as those equipped with catalytic converters.

12. Development of Methods for the Determination of Toxic Organic Compounds in Aqueous Leachates of Hazardous Wastes and Development of a Quality Assurance Sludge Material (14215, 14626)

D. P. Enagonio, L. R. Hilpert, C. R. Vogt

Over the past few years, increasing concern has been expressed over the potential adverse environmental and health effects associated with hazardous wastes. The Resource Conservation and Recovery Act of 1976 requires the identification of hazardous wastes based, in part, on chemical characterization of the waste and, in part, on the mobility or leachability of toxic chemical components of the waste. During the past year, we have developed measurement methods for the analysis of toxic organic compounds in aqueous leachates of hazardous wastes and methods for the preparation and analysis of a quality assurance sludge material.

One of the several promising processes for the conversion of coal to liquid fuels is the solvent refined coal (SRC II) process. One aspect of the process still under investigation is the handling of the vacuum still bottom solid waste material. An SRC II vacuum still bottom material was characterized by gas chromatography/mass spectrometry (GC/MS). A sample of ground material was extracted with methylene chloride, and an aliquot of this extract analyzed by GC/MS on a 30 m SE-52 fused silica capillary column. The total ion chromatogram is shown in figure 32. Most of the peaks identified were polynuclear aromatic hydrocarbons (PAH).



(a)	phenanthrene	
(b)	anthracene	
(c)	Carbazole & C_1-subst phenanthrene/anthracene	
(d)	C_1-subst phenanthrene/ anthracene	
(e)	fluoranthene	
(f)	pyrene	
(g)	C_1-subst fluoranthene/pyrene	
(h)	C_1-subst fluoranthene/pyrene	
(i)	C_1-subst fluoranthene/pyrene	
(j)	m/e 252	
(k)	benz[a]anthracene	
(l)	chrysene/triphenylene	
(m)	m/e 252	16 isomers
(n)	m/e 252	
(o)	m/e 266	15 isomers
(p)	m/e 266	
(q)	m/e 266	
(r)	m/e 252 benzofluoranthene	
(s)	benzo[e]pyrene	
(t)	benzo[a]pyrene	
(u)	perylene	
(v)	m/e 266	
(w)	m/e 278	12 isomers
(x)	m/e 276	9 isomers
(y)	m/e 276	
(z)	m/e 276	
(aa)	m/e 276	
(bb)	m/e 290	
(cc)	m/e 276	
(dd)	m/e 290	15 isomers
(ee)	m/e 290	
(ff)	m/e 290	

Figure 32. Total ion chromatogram of CH_2Cl_2 extract of SRC II vacuum still bottoms material.

Aqueous leachates of a homogenized SRC II vacuum still bottom material (particle size 250 µm) were prepared using the EPA (dilute acetic acid) leach procedure [1], and the ASTM-A (distilled water) leaching method [2]. The leachates were carried through a solvent extraction scheme to isolate the acids and base-neutral compounds. The extraction scheme was developed and tested using a series of synthetic aqueous leachates. The method efficiently extracted 20 target analytes from water at the 10 µg/L level. The organic extracts of the SRC II vacuum still bottom leachates were analyzed by GC/MS in the selected ion monitoring (SIM) mode for quantitation, and the full scanning mode for confirmation of identifications. The results of the quantitative determinations are shown in Table 29.

Table 29. Concentrations of Compounds in Bulk Aqueous Leachates of SRC II Vacuum Still Bottom Material.

Analyte	Concentration (μg/L)[a] ASTM-A Leachate	Concentration (μg/L)[a] EPA Leachate[b]
2-picoline	0.24	ND[c]
phenol	6.68	1.09
o-cresol	1.63	0.18
naphthalene	0.38	0.20
quinoline	0.39	ND
1,4-naphthoquinone	0.15	0.08
dibenzothiophene	0.02	ND
phenanthrene	0.06	0.05
carbazole	0.76	0.46
fluoranthene	0.02	0.02

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[a] Values are the average of two determinations.

[b] This is commonly referred to as the EP leach procedure.

[c] Not detected.

The direct hydrogenation process for the conversion of coal to liquid products is known as the H-coal process. Aqueous leachates of a solid waste from the H-coal process were also extracted and analyzed by GC/MS. Concentrations of organics in the H-coal leachate we examined (see Table 30) were significantly higher than in the leachate of the SRC II vacuum still bottom material. It should be noted that the wastes we examined may not be representative of the SRC II and H-coal processes in general. The H-coal sludge is being analyzed by five laboratories to determine the interlaboratory variability in the leaching and analysis of a waste material. The results from this study will help to refine methods for the leaching and analysis of hazardous wastes.

Work was initiated this year on the preparation and analysis of a quality assurance sludge for the EPA. The initial step involved selection of a suitable sludge material. Selection criteria included: 1) a material which contained "toxic" organic compounds at trace levels (1-50 ppm); 2) a material in which the target analytes were stable; and 3) a material which could be analyzed with current EPA methodology.

Table 30. Concentrations of Compounds in EPA Leachates of H-Coal Material.

Analyte	Conc. (μg/L)[a]	Analyte	Conc. (μg/L)[a]
picoline	ND[b]	1-naphthylamine	2.6 ± 0.3
phenol	241 ± 20	4-aminobiphenyl	ND
o-cresol	97 ± 6	dibenzothiophene	4 ± 1
naphthalene	257 ± 9	phenanthrene	71 ± 13
quinoline	34 ± 8	carbazole	322 ± 44
1,4-naphthoquinone	ND	fluoranthene	10 ± 4
acenaphthylene	ND	benz[a]anthracene	2.4 ± 0.6
2-naphthol	12 ± 0.1		

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[a] Values are the average of three determinations ± the standard deviation based on 2 degrees of freedom.

[b] Not detected.

A liquid waste has been selected for analysis. The following target analytes are to be determined in the sludge: phenol, m-dichlorobenzene, pentachlorophenol, hexachlorobenzene, phenanthrene, fluoranthene, benzidine, pyrene, n-propyl phthalate, benz[a]anthracene, and dioctyl phthalate. The target analytes are not natively present in the sludge, therefore, the material will be fortified by addition of the compounds to bring the concentrations within the 10-50 ppm range.

A gas chromatographic method utilizing high-resolution capillary columns with flame ionization detection has been developed for quantitative measurement of all of the analytes, except the phenol and m-dichlorobenzene. These compounds will be determined by GC/MS with selected ion monitoring. Plans for next year include an interlaboratory comparison to evaluate variability and laboratory accuracy in the analysis of this liquid sludge.

References

[1] "Test Methods for Evaluating Solid Wastes: Chemical/Physical Properties," Federal Register 45: 98; May 19, 1980.

[2] "Proposed Methods for Leaching of Waste Materials," 1979 Annual Book of ASTM Standards, Part 31.

13. GC/MS Determination of Acidic and Basic Compounds in a Shale Oil Process Water (11320)

L. R. Hilpert, K. L. Richie

Over the past few years, there has been an increasing concern over the potentially toxic compounds associated with the processing of alternate fuels. Some of these organic compounds may eventually be transported into the environment as gaseous or liquid effluents. In order to evaluate potential environmental impact, feedstocks, process streams, fuels, and effluents must be analyzed for their trace organic compound content. The results of these analyses cannot be evaluated without knowing the accuracy of the analytical data obtained. To begin assessing the accuracy of the methodology and analytical data, we have developed interlaboratory comparison materials which can be used to assure comparability among U.S. Department of Energy laboratories and NBS. The participating laboratories, known as the DOE/NBS Analytical Characterization Group, regularly conduct studies in the quantitative analysis of trace organic constituents in materials such as shale oil, solvent refined coal, and aqueous effluents obtained during production of these alternate energy sources. The participants also meet to discuss the strengths and weaknesses of the analytical methods as well as results of interlaboratory comparison studies.

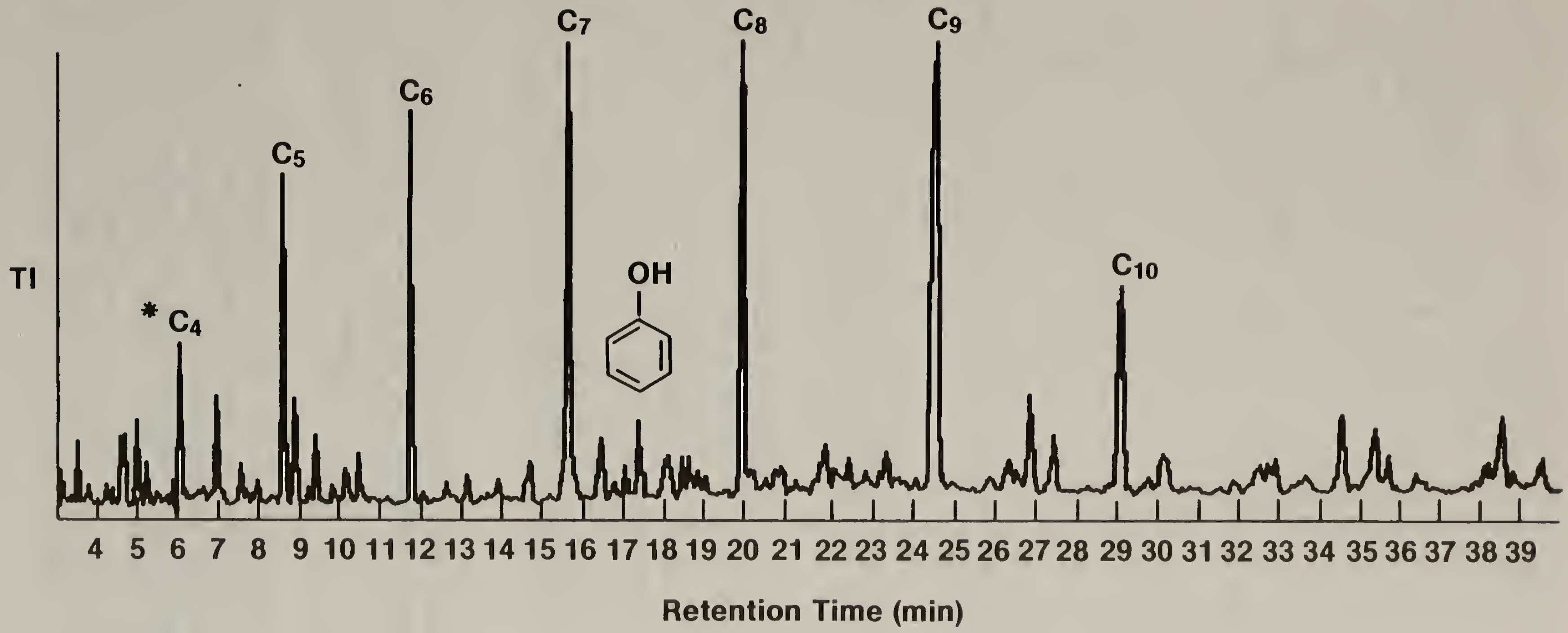
As a result of discussions held at recent Analytical Characterization Group meetings, the DOE/NBS program is currently focusing on intercomparison studies of a shale oil process water. High resolution capillary column gas chromtography/mass spectrometry (GC/MS) with selected ion monitoring has been used to quantitate organic acids and bases at the μg/mL level in a shale oil process water.

Process water, which was obtained from a simulated *in situ* retort, was subjected to simple acid/base extractions to isolate basic and acidic components. The extracts were concentrated and analyzed by GC/MS. Figure 33 shows a total ion chromatogram of the organic acids extracted from the process water. The normal aliphatic acids and phenol are identified.

Quantitative determinations were made by GC/MS with selected ion monitoring using a standard addition technique. NBS results are listed in Table 31 together with the results reported by the other participating laboratories. Results by our laboratory for the basic compounds are listed in Table 32. Results from the participating laboratories have not been reported at this time.

As seen in Table 31 there is a wide range among the values reported by the various laboratories, which strongly emphasizes the need for the continuing development of accurate analytical methodology and for interlaboratory comparisons.

The Analytical Characterization Group will meet in November to discuss and compare the results and methods used in current analyses as well as to decide upon the next material for an interlaboratory comparison study.



*C_4–C_{10} represent n–aliphatic acids.

Figure 33. Total ion chromatogram of GC/MS analysis of organic acids and phenol in a shale oil process water.

Table 31. Interlaboratory Comparison of Shale Oil Process Water Analysis.

	Concentrations (μg/mL)					
	NBS	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
n-Butanoic acid	50±8[a]	17.0	70±12	95	52	82.3±7.4
n-Pentanoic acid	72±9	--	--	130	90	--
n-Hexanoic acid	88±4	54.6	107± 5	160	91	86.4±8.6
n-Heptanoic acid	149±9	--	--	--	94	--
n-Octanoic acid	140±8	--	--	--	96	--
n-Nonanoic acid	82±5	--	--	--	62	--
n-Decanoic acid	38±2	--	--	--	23	--
Phenol	16±4	31.6	32± 4	25	19	17.2±1.2

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[a] Precision expressed as one standard deviation of the mean for three standard addition experiments.

Table 32. NBS Analytical Results for Basic Compounds in a Shale Oil Process Water.

Compound	Concentration (μg/mL)
Aniline	1.3 ± .2[a]
2,4,6-Trimethylpyridine	21.7 ± 1.8
Isoquinoline	.8 ± .06

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[a] Precision expressed as one standard deviation of the mean for three standard addition experiments.

14. Development of an Isotope Dilution/Mass Spectrometric Definitive Method for the Determination of Serum Urea (11320, 14306)

A. Cohen, H. S. Hertz, R. Schaffer, L. T. Sniegoski, M. J. Welch,
E. White V, W. T. Yap

Definitive methods provide the clinical chemistry community with an accuracy base to which reference, and ultimately, field methods can be compared. We have been involved for several years in the development of definitive methods for organic serum analytes and have successfully developed such methods for cholesterol, glucose, and uric acid. Another clinically important analyte is serum urea, which is used as a measure of kidney function and in protein metabolism studies. Work has now been completed on a method for serum urea which is of sufficient accuracy and precision to be considered a definitive method.

This method utilizes isotope/dilution mass spectrometry, as have all of the other definitive methods for organic serum analytes. A brief description of the method is as follows: A weighed quantity of urea-^{18}O is added to a known weight of serum such that the labeled/unlabeled urea ratio is near 1:1. After an equilibration period, the sample is freeze-dried and the urea is extracted from the residue and sublimed. The sublimate is added to a mixture of diketene and glacial acetic acid in a vial, which is then sealed and heated at 82-84 °C for two days. Under these conditions urea is converted in high yield to 6-methyluracil. After the solvent and unreacted diketene are evaporated, bis(trimethylsilyl)acetamide is added to convert the product to 6-methyluracil-diTMS. Calibration standards, consisting of known amounts of the labeled urea-^{18}O and pure Standard Reference Material (SRM) 912, Urea, are also converted to the derivative. For each sample, the two standards, whose unlabeled/labeled weight ratios most closely bracket that of the sample, are selected. The sample and its two standards are injected onto a 30-meter SE-30 SCOT gas chromatographic column operated at 125 °C in the following sequence: One standard is injected, followed 5-1/2 minutes later by the sample and 11 minutes later by the other standard. After a 25 minute retention time, the ion abundance ratios for the $(M-15)^+$ ions at m/z 255 (unlabeled) and 257 (labeled) are measured for each of the three peaks. Measurements are made in the electron impact (EI) mode at 70 eV, utilizing magnetic field switching. The ratio from the sample is compared, using linear interpolation, with the ion abundance ratios from the standards to find the quantity of unlabeled urea in the sample. For each sample, measurements are repeated, on a second day with the order of standards reversed, and the mean of the two days' measurements is taken as the reported result.

Because of contributions of the labeled urea derivative at the mass monitored for the unlabeled derivative, and vice versa, the relationship between weight ratios and ion abundance ratios is not truly linear. A mathematical study was performed to find the maximum error possible when linear interpolation was used with our bracketing standards. The worst case, which occurs when the ratios of the two standards are the farthest apart and the bracketed sample falls midway between the two, was found to be less than 0.04 percent for our standards. Thus linear interpolation can be used without correction. A description of this mathematical study has been submitted for publication in Biomedical Mass Spectrometry.

The method was used to measure urea levels in both freeze-dried and frozen serum pools. Three sets of samples were prepared from SRM 909, a freeze-dried human serum pool. Each set consisted of two samples from each of three vials of SRM 909. The results are summarized in Table 33, including the overall mean value which is the certified concentration for the SRM.

As a test for hidden interferences in the above measurement conditions, two samples from each set were remeasured using different pairs of ions; first, EI measurements of the $(M-30)^{++}$ ions at m/z 120 and 121, and second, chemical ionization (CI) measurements of the $(M+1)^+$ ions at m/z 271 and 273. These results, along with the previous results for those six samples, are shown in Table 34.

Table 33. Urea Levels Found in the Human Serum SRM by the ID/MS Definitive Method (6 samples per set).

Set	Mean mg urea/g serum pellets	CV %
1	7.236	0.07
2	7.249	0.17
3	7.247	0.06

Statistical Summary: Mean = 7.244; CV's - replicates 0.14%, sets 0.10%, reproducibility 0.17%. Standard error of average = .00439, CV = 0.06%.

Table 34. Urea Levels Found in Six Human Serum SRM Samples Using Three Different Pairs of Ions.

Ions Measured	Mean mg urea/g serum pellets	CV %	% Difference from (255/257) Results
255/257	7.242	0.12	
120/121	7.239	0.12	-0.05
271/273	7.240	0.12	-0.03

The urea level was also measured in five frozen serum pools from a Centers for Disease Control round robin study. Three sets, each consisting of one sample per pool, were independently prepared. The results are shown in Table 35.

Table 35. Urea Levels Found in Five Round Robin Frozen Serum Pools by the ID/MS Definitive Method.

Pool	Mean mg urea/g serum	CV %
Control 1	.2393	0.13
Control 2	.8828	0.14
Unknown 7	1.525	0.23
Unknown 8	.3564	0.13
Unknown 9	.8259	0.15

One sample from each pool was remeasured using the alternate ions. The mean differences from the results for the 255/257 ions were +0.03 percent for the 120/121 ions and +0.01 percent for the 271/273 ions. These pools were also analyzed at CDC by the coupled-enzyme candidate reference method. Their results for the five pools differed from our results by -0.58 percent to +1.15 percent, differences which are small compared with the imprecision of their measurements, thus providing strong evidence that no serious systematic bias exists between the two methods.

For a method to be considered definitive, the results must be free of significant bias and be of high precision. This ID/MS method for urea has provided high precision results for both freeze-dried and frozen serum. Confirmatory measurements at alternate ions demonstrate that no significant biases exist among the three measurement conditions. Thus the probability of a hidden interference is very small, since such an interference, to remain undetected, would have to co-elute with the 6-methyluracil-diTMS and contribute proportionally the same at the three ions measured. No other source of significant bias has been found, therefore, the requirements for a definitive method have been satisfied. A manuscript describing the method is in preparation.

Development of definitive methods for creatinine and triglycerides is in progress and a method for digoxin is in the planning stage. Each method developed will be used to certify the concentration of the corresponding analyte in the Human Serum SRM.

15. Improved Instrumentation for Organic Isotope Dilution/Mass Spectrometry Measurements (11320, 14301)

S. Meiselman, F. Ruegg (550), R. Shideler (550), M. J. Welch, E. White V

Our ongoing project to develop definitive methods for organic serum analytes requires instrumentation of high stability to provide the necessary precision. All of our work to date has been with serum analytes present in relatively high concentrations. As future work turns to analytes in lower concentration, our instrumentation must be even more stable than before, if we are to continue successful development of definitive methods. Our approach to improved instrument stability has been to seek to upgrade existing instrumentation, rather than to purchase costly, new systems. In recent years, upgrades have included replacement of the mass spectrometer source diffusion pump with a turbomolecular pump for reduction of pressure fluctuations, installation of a pressure regulated flow system in the gas chromatograph, installation of a variable splitter at the head of the GC column, and the use of fused silica tubing for the transfer line in the GC/MS interface.

Recently we have replaced both the multiple ion monitoring system and our old data handling system with a new system assembled principally from components available in the NBS storeroom. The new system, diagrammed in figure 34, is designed to provide computer control for certain instrument parameters which have to be rapidly and reproducibly changed, as well as to handle data acquisition and reduction. A 64 K microcomputer controls switching of the magnetic field for each measurement cycle, through a 16 bit digital-analog converter (DAC). After each switch of the magnetic field, the computer waits for a signal indicating that the field has stabilized before generating a triangular waveform through a ±150 volt power supply. This waveform, whose frequency and amplitude are computer controlled, is sent to the mass spectrometer detector beam deflection plates a preset, integral number of times for each measurement cycle. This provides for more reproducible data acquisition than achieved with the old system in which the waveform was generated continuously and the measurement began at random points across the waveform. The ion intensity signal generated by the electron multiplier is fed through a solid state

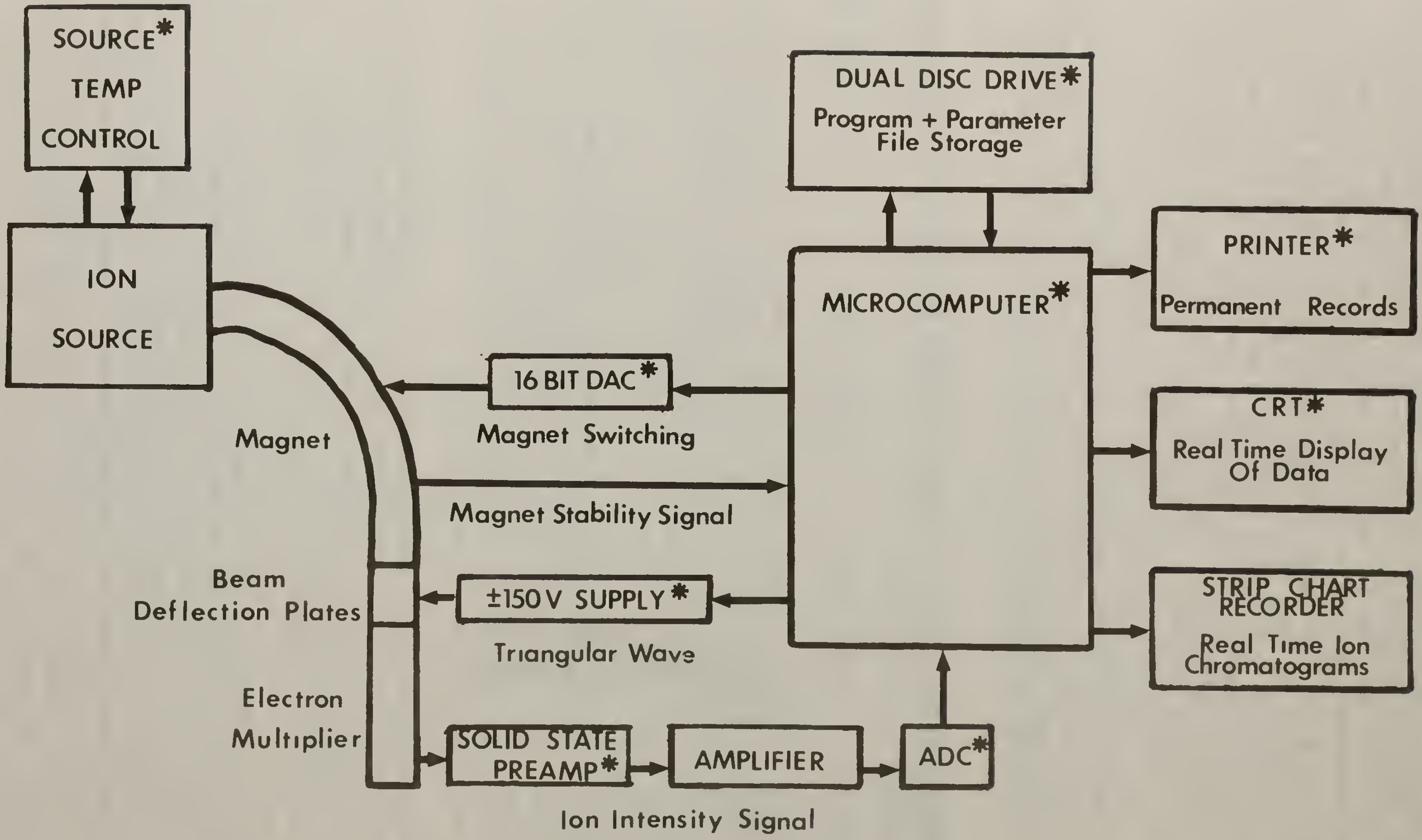

Figure 34. Diagram of the upgraded organic isotope dilution mass spectrometer system.
*New components.

preamplifier, built at NBS, which provides better stability and linearity of response than the vacuum tube device which came with the mass spectrometer. The signal, after passing through the original amplifier for the mass spectrometer, is digitized by an analog-digital converter (ADC). The computer generates two real-time displays of the data; numerical data is shown on a CRT, and an analog signal is sent to a strip chart recorder for display of the ion chromatograms for the unlabeled and labeled species. After data acquisition is complete for each sample, the computer corrects the accumulated data for baselines measured before the elution of the analyte and calculates the ratio of the corrected ion abundances of the labeled and unlabeled species. The ratios are displayed on the CRT and the accumulated counts and ratios are fed to a printer for permanent record. The computer is interfaced to a dual disc drive for access to operating programs, and parameter files for each analyte.

The new system exhibits improved precision and greater reliability, enabling us to measure serum urea levels with an overall relative precision of 0.17 percent, compared with 0.2-0.4 percent overall precisions for cholesterol and glucose with the old system. The computer provides the capability of controlling other instrumental parameters and modifying our data acquisition and reduction as necessary.

Our most recent system upgrade has been installation of an NBS-built circuit to control the ion source temperature in the mass spectrometer. Previously, the ion source temperature changed while measurements were being made and corrections were through manual adjustments in the heater current. The new circuit senses the temperature in the source and adjusts the heater current appropriately. This improvement simplifies the operator's task and we also expect it to make ion source conditions more stable, leading to better precision.

Plans for further improvements include acquisition of an electron-impact-only ion source for the instrument to use in conjunction with our combined electron-impact chemical-ionization source. Such a source, optimized for one mode of ionization, is expected to provide more stable operation in that mode than is possible with the combination source. We also plan to test a new ion selection method in which the magnetic field is held constant and the ion beam is switched at the deflection plates. Such a system should allow for less delay time between measurement cycles since magnetic hysteresis effects, which now limit the switching rate, will be avoided. The major effort required for this new technique is the generation of the necessary software for the existing system.

16. Preparation of Solutions of Stable Isotope Labeled Marker Compounds for Use in the Analysis of Priority Pollutants (14220)

J. M. Brown-Thomas, S. N. Chesler, D. P. Enagonio, F. R. Guenther, W. F. Kline, W. E. May, R. M. Parris, R. E. Rebbert, L. T. Sniegoski, E. White V

A "Master Analytical Scheme" being developed by contractors of the Environmental Protection Agency is intended to allow qualitative and quantitative analysis of priority pollutants in water by gas chromatography/mass spectrometry. This scheme provides for the analysis of "purgeable," "extractable," and "intractable" organic compounds in surface and drinking water and in industrial, energy-related, and municipal effluents. Nominal lower quantifiable limits are 0.1 μg/L for drinking water, 1 μg/L for surface water, and 10 μg/L for effluents. A similar "Comprehensive Scheme for Soils, Sediments, and Sludge" is also being developed. For use in these analytical schemes, NBS has developed internal standards consisting of solutions of deuterated organic compounds in water or methanol. The standards are to be added to a specified sample volume. For analysis of "purgeables," 1 μL of the standard solution in methanol in a 1 μL disposable glass capillary pipet sealed in a melting point tube is added to 250 mL of sample, and the melting point tube and pipet are crushed to add the deuterated standards to the sample. For analysis of "extractables" and "intractables," 5 to 10 mL of marker compound solution from a sealed ampoule is added to a 1 or 2 L sample. From March 1980 to July 1982, 33 sets of marker compound solutions, "purgeables," "extractables," and "intractables," were prepared and from 40 to 100 ampoules of each set were shipped to EPA.

From each set of standards prepared, approximately 20 ampoules were retained by NBS for studies of stability and homogeneity. Analysis by gas chromatography and liquid chromatography of sets prepared in March - June 1980 and in February - April 1981 showed no significant instability or inhomogeneity (vial-to-vial variation) during storage at 4 °C for up to eleven months.

The most recently prepared marker compound solutions, prepared in July 1982, were the first made for the "Comprehensive Scheme for Soils, Sediments, and Sludge." These sets contained 19 deuterium-labeled compounds and one non-deuterated fluorine-containing compound. One of the deuterium-labeled compounds, 2-naphthalene-d_7-sulfonic acid, was not commercially available and was synthesized at NBS. The concentrations of the sets are given in Table 36. Sixty ampoules of each set will be shipped to EPA.

All compounds used in the marker compound solutions were checked for chemical purity by mass spectrometry and by either gas chromatography or liquid chromatography, as well as for isotopic purity by mass spectrometry.

Table 36. Marker Compound Solutions for Use in the "Comprehensive Scheme for Soils, Sediments, and Sludges".

Compound	Concentration in Sample after Addition of Standard (µg/L)	
	Set 1	Set 2
PURGEABLES[a]		
Naphthalene-d_8	5.0	49.1
Anisole-d_3	2.2	27.1
Chlorobenzene-d_5	4.6	4.3
Bromoethane-d_5	0.45	5.1
STRONG ACID EXTRACTABLES[b]		
Benzoic-d_5 acid	0.99	104.0
Heptanoic-d_{13} acid	10.0	99.5
EXTRACTABLES[c]		
o-Xylene-d_{10}	2.0	108.0
Nitrobenzene-d_5	105.5	517.7
Naphthalene-d_8	21.5	498.8
Acridine-d_9	19.4	99.5
Phenol-d_6	96.1	387.8
Propiophenone-d_5	--	104.5
1-Phenyl-d_5-ethanol	--	518.2
Perylene-d_{12}	1.2	98.2
Acetophenone-d_5	--	104.1
NEUTRAL INTRACTABLES[d]		
t-Butanol-d_9	117.1	581.2
Nitrobenzene-d_5	21.6	103.7
IONIC INTRACTABLES[d]		
n-Butyl-d_9-amine	120.2	553.0
n-Butyric-d_7 acid	7.9	547.2
2-Naphthalene-d_7-sulfonic acid•H_2O	105.5	508.5
N-Ethyl-2-fluorobenzylamine	107.2	525.8
2-Phenylethyl-d_4-amine	103.7	513.3

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[a] 1 µL solution in methanol added to 250 mL sample.

[b] 5 mL solution in methanol added to 2 L sample.

[c] 5 mL solution in methanol added to 1 L sample.

[d] 7.5 mL (Set 1) or 10.0 mL (Set 2) aqueous solution added to 1 L sample.

17. Surface-Enhanced Raman Spectroscopy of N-Methylpyridinium Cation and Pyridine: Identification of Surface Species (51101, 51301)

K. A. Bunding, R. A. Durst

There has been considerable controversy over the mechanism of the surface-enhanced Raman scattering (SERS) effect and the identification of the species producing the enhancement. Since not all molecules show enhancement, the role of particular enhancing sites as well as molecular orientation and molecule-surface interactions seemed to be very important to the explanation of the phenomenon.

We have reported SERS from N-methylpyridinium iodide (NMPI) solutions in contact with a silver electrode [1]. Since most molecules which show surface enhancement in an electrochemical cell (e.g., pyridine, piperidine, carboxylates, and cyanide) have unshared pairs of electrons, the observation of SERS in the N-methylpyridinium cation (NMP^+) was significant. However, attempts to obtain SER spectra from N-methylpyridinium chloride (NMPCl) solutions at a potential of -0.6 V were unsuccessful until trace amounts of iodide were added [1]. This result implies a major role for the iodide ion either in the enhancement mechanism itself or in promoting adsorption of the cation, perhaps via co-adsorption or the formation of a surface complex.

A series of experiments was undertaken to clarify the role of the anion in SERS measurements involving the NMP^+ cation and to identify the actual surface species observed in such experiments. We have examined the effect of varying the anion, the pH, and the electrochemical potential; we have performed competition experiments in which both pyridine (py) and NMP^+ were present in the electrolyte; and we have compared the ordinary Raman spectrum of the solid silver-pyridine complex $Ag(py)_2NO_3$ with the various SER spectra obtained.

The SER spectra of NMPBr and NMPCl, unlike NMPI, show bands that are due to pyridine as well as NMP^+. Since there is no pyridine initially present in the solution and there is no electrochemical reaction in the potential range studied, this must be due to decomposition of the NMP^+ to pyridine by surface-induced and/or photochemical reactions. The decomposition theory is further supported by the increase in relative intensity of the pyridine bands with time.

Competition experiments performed with both pyridine and NMP^+ in the solution confirmed the presence of pyridine bands in the SER spectra of NMPBr and NMPCl and their absence in NMPI spectra. Apparently the I^- is more selective for the organic cation. Thus, even if NMPI were to decompose to pyridine, this would not be observable. In order to assign the new bands in the NMPBr and NMPCl spectra to pyridine, the spectra of the silver-pyridine complex, $Ag(py)_2NO_3$, pyridine in solution and the SER spectra of pyridine at -0.2 and -0.6 V were taken. This allows a clear assignment of H-bonded pyridine bands and Lewis-coordinated pyridine bands. We see in the spectra at the more positive potential, -0.2 V, both Lewis- and H-bonded pyridine and at -0.6 V, only H-bonded pyridine.

The spectrum of pyridine in KI at -0.35 V is very different from that in KCl. This suggests that in KI the silver Lewis-acid sites are not available to pyridine or are somehow modified; also the H-bonded species is not enhanced. The lack of enhancement for the solution species suggests that the enhancement mechanism is not effective beyond the double layer.

By studying the effects of anion, pH, and potential variations and by competition experiments, we have demonstrated that different pyridine/pyridinium species are responsible for the observed spectra. In addition, it appears that surface-induced and/or photochemical reactions may produce species not originally present in the sample solution. It is also clear from this work that care must be exercised in assigning SER bands to sample components without consideration of possible decomposition to other species.

Reference

[1] Bunding, K. A.; Bell, M. I.; Durst, R. A. Chem. Phys. Lett. *89*, 54 (1982).

18. *Electrochemical and Spectroelectrochemical Studies of Copper and Iron Bleomycin Complexes* (51101)

M. L. Fultz

The bleomycins are a family of structurally similar glycopeptide antibiotics that are isolated as copper complexes from the bacterial strain *Streptomyces verticillus*. Bleomycin exhibits antitumor activity and has been used to treat squamous cell carcinomas, lymphomas, and testicular carcinomas. *In vitro*, bleomycin exhibits DNA-strand scission when bound with iron and oxidized by molecular oxygen. However, its *in-vivo* action is not clearly understood. Current studies have not resolved the fundamental question of whether there are several distinct pharmacological agents among bleomycin and its complexes or whether there is a single proximate agent *in-vivo*.

To more clearly define the role of the metal ion in the mechanism of bleomycin action, a study of the redox properties of the copper and iron complexes has been undertaken. A previous study of copper bleomycin found the copper reduction to be irreversible at a carbon paste electrode. Attempts to use coulometry to determine the number of electrons involved in the reduction were not successful. Our studies have shown copper bleomycin to exhibit electrochemically irreversible reduction at mercury and glassy carbon electrodes at approximately -0.53 V *vs*. SCE and pH 7. Copper bleomycin exhibited no electroactivity at platinum and gold electrodes. The cyclic voltammograms also showed a redox couple at more positive potentials close to the Cu(II)→Cu(0) couple. Thin-layer coulometry at a mercury-gold minigrid electrode gave an n value of 1.3. Atomic absorption analysis of the electrode used for the coulometry showed that it contained 100 times the background level of copper metal. The following mechanism has been proposed to account for these observations:

$$\begin{tikzcd} \mathrm{Cu(II)\text{-}Blm} \arrow[r, "e^-"] & \mathrm{Cu(I)\text{-}Blm} \arrow[r, shift left] & \mathrm{Cu(I)+Blm} \arrow[l, shift left] \arrow[d] \\ & & \mathrm{Cu(metal)} \end{tikzcd}$$

A pH study of copper-bleomycin showed more negative reduction potentials with increasing pH. This agrees with the hypothesis that reduction of one of the amine ligands is necessary for reduction of the copper.

Iron-bleomycin exhibits quasi-reversible redox behavior at glassy carbon electrodes. In order to study the spectroelectrochemistry of iron-bleomycin, we constructed an optically transparent electrode consisting of reticulated vitreous carbon with a pore size of 100 pores/square inch. This electrode exhibits thin-layer behavior because of the small size of the pores. By monitoring the 384 nm absorption band of iron(III)-bleomycin, the oxidation and reduction of iron-bleomycin was monitored. The concentrations of oxidized to reduced species at various potentials applied to the electrode were calculated. Nernst plots of the data show a one electron reduction with a formal potential at pH 7 of -0.090 V vs. SCE. This agrees well with values obtained by spectrophotometric titrations.

19. Polymer Modified Electrodes: Electrocatalytic Sensors for Detection of Organic Analytes (14625, 51101)

E. A. Blubaugh, Jr.

Polymer modified electrodes may provide sensors which will allow the selective and sensitive detection of organic analytes (organohalides, etc.). Polymer films offer the advantages of inherent chemical and physical stability, incorporation of large numbers of catalytic sites, and relatively facile electron transport across the film.

We have followed two approaches in polymer film electrode fabrication. These are electrochemical initiated polymerization and spin-dip coating. These two approaches allow a much greater degree of flexibility in polymer film type, thickness and morphology. However, the most important aspect is that we are given a greater latitude in the subsequent mode of catalyst immobilization.

The most challenging area of investigation is the behavior of charged or uncharged film penetrants. The ultimate catalytic efficiency of these polymer film electrodes will depend to a large degree on the influx of these substrate molecules across the film interface.

We have started both theoretical and experimental investigations, which we hope will shed light on the factors which influence diffusion of substrate molecules in the polymer films. Some of these factors are solvent, degree of solvation, electrode potential, and charge, if any, on the penetrant.

Polymer films of $[Ru^{II}(bipy)_2(4\text{-}VP)_2]\cdot 2PF_6$ (where bipy is bipyridine and VP is vinyl pyridine) have been obtained via electrochemical initiation of an anionic polymerization of the vinyl monomer. Ruthenium bipyridyl complexes show very interesting and potentially exploitable (catalytic films) excited state chemistry.

$$Ru^{II}(bipy)_3 + h\nu \rightarrow Ru^{III}(bipy)_2(bipy)^{\dot{-}}$$

The transient excited state molecule is both a powerful oxidant and reductant and allows the photocatalytic oxidation or reduction of organic solution species. Polymer films of $Ru^{II}(bipy)_2(4\text{-}VP)_2$ have been obtained, characterized, and electrochemically evaluated. These films have shown very facile electron transfer through the film and have demonstrated catalytic oxidation of organic carboxylates. This reaction does not take advantage of the abovementioned photocatalytic reaction. The ECC reaction mechanism (i.e., electron transfer followed by two subsequent chemical reactions) for the oxidation of organic carboxylates occurs in the following steps. The electron transfer reaction oxidizes the ruthenium in the complex from II to III. The ruthenium(III) complex then catalytically oxidizes the carboxylate to the radical anion ($\dot{CO_2^-}$) which undergoes further reaction with the Ru(II) complex to produce a Ru(II) bipyridyl radical anion. This radical anion in turn produces a visible luminescence during the annihilation reaction with the Ru(III) complex. The luminescence resulting from the annihilation of the oxidized and reduced components should allow the very sensitive detection of $R\text{-}CO_2^-$ components.

We have utilized these $Ru^{II}(bipy)_2(4\text{-}VP)_2$ polymer films in the evaluation of the role and relative influence that migration plays in the "diffusional" current-time response of these polymer film electrodes. This area of research is being pursued and computer-controlled equipment will be completed soon to allow this study to be further explored.

The immobilization of cationic (organic and inorganic) catalysts also has been demonstrated. We have immobilized these cationic species within a cation exchange polymer. The immobilization scheme is performed in two steps: spin-dip coating of the polymer onto the electrode and subsequent cation exchange of the catalyst of interest. These films have shown electrochemical response with cations such as methyl viologen, methylene blue, and $Ru^{II}(bipy)_3$. Preliminary results indicate that the methyl viologen modified electrode shows evidence for the catalytic oxidation of organohalides.

20. Theoretical Analysis of Charge Transport in Polymer-Modified Electrodes (51101)

W. T. Yap

In studies of electrochemistry using polymer-coated electrodes, there are indications that the transport of the charged electroactive species through the polymer layer may take place not only by diffusion due to concentration gradients, but also by migration due to the potential gradient. We have made a theoretical analysis for chronoamperometry using polymer-coated electrodes, taking into account the effects of diffusion and migration in a constant potential gradient, i.e., constant electric field. Equations were developed for the concentration distributions of the charged electroactive species and for the current, Ψ, as a function of time, t. Figure 35 shows the product $\Psi\sqrt{t}$ as functions of $\sqrt{t}$. Curve 4 is for the case where the transport is only by diffusion, i.e., no migration effect. The horizontal portion at short time for curve 4 corresponds to the classical behavior described by the Cottrell

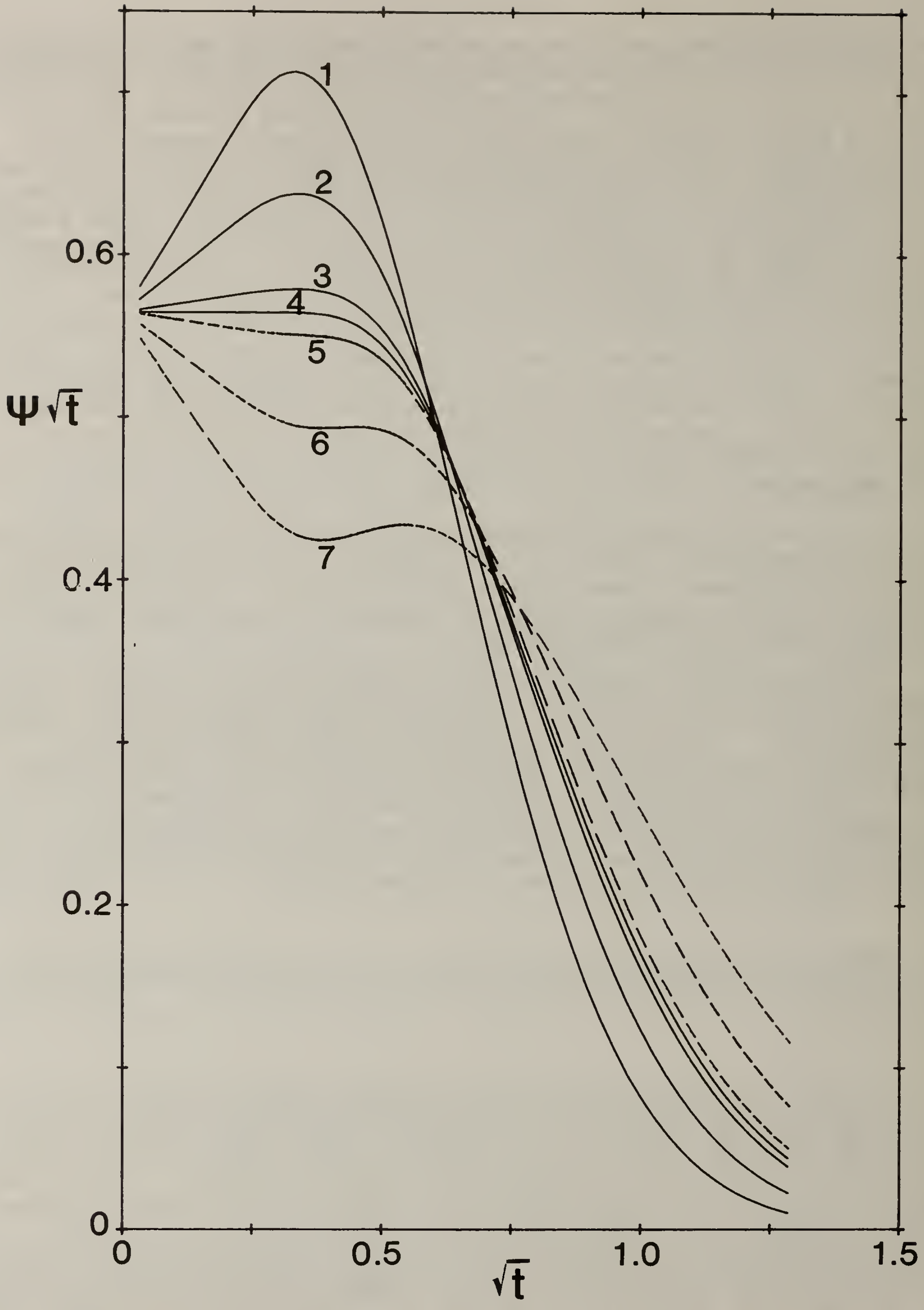

Figure 35. Plot of the product of current and square root of time <u>vs</u>. square root of time for several values of constant electric fields.

equation. Curves 1 to 3 show cases where the diffusion current is augmented by the migration current, the electric field decreases from curve 1 to curve 3. Curves 5 to 7 depict the cases where the migration current opposes the diffusion current, the electric field increases from curve 5 to curve 7. Preliminary results from experiments using poly-Ru-vinyl bipyridine show curves similar to that of curves 1 to 3.

A paper will be published wherein we will present the theory and also give a procedure for estimating the apparent diffusion coefficient and the ionic mobility of the charged electroactive group from the current-time curve [1].

Reference

[1] Yap, W. T,; Durst, R. A.; Blubaugh, E. A.; Blubaugh, D. L. J. Electroanal. Chem. (in press).

21. Characterization of an Angiotensin I SRM by Proton NMR Spectroscopy at 400 MHz (14306)

B. Coxon, S. A. Margolis

The high sensitivity and dispersion of the WM-400 NMR spectrometer have allowed it to be used in certification of the Angiotensin I SRM in two ways. Solutions for analysis by proton NMR were conveniently prepared by dissolution of a single unit (0.5 mg) of the SRM in 100 percent deuterium oxide (0.5 mL). Under these conditions, suppression of the HOD signal was not necessary, and spectra with good signal:noise ratio were obtained by signal averaging of 2,000 scans.

The major non-peptide impurity (or counterion) in the Angiotensin I SRM is acetate and, therefore, a method was developed for analysis of acetate content by proton NMR. Because the acetate methyl proton signal at δ 1.922 was found to overlap some of the proton signals of the angiotensin I (see figure 36), an acetate-free sample of angiotensin I was prepared first, in order to determine an accurate proton count for the signals underlying the acetate peak. Removal of the acetate from the sample was achieved by two lyophilizations of the material with 0.01 mol/L hydrochloric acid. Analysis of this sample by proton NMR indicated that it was indeed free of acetate and that the proton count in the spectral region of interest was three. Thereafter, the samples of the SRM were analyzed without lyophilization, and the appropriate value of the spectrum integral for the three protons was subtracted from the total integral of the acetate methyl peak and its underlying signals, in order to obtain the integral of the acetate peak. The appropriate value of the integral for three protons was determined by averaging of the integrals of a total of 29 proton signals in the high field region, including many of those that originated from the methyl, methylene, and methine protons of angiotensin I. Proton NMR determinations on six samples of the SRM yielded a mean acetate content of 1.36 ± 0.08 (± one standard error) molecular equivalents of acetate per mole of angiotensin I.

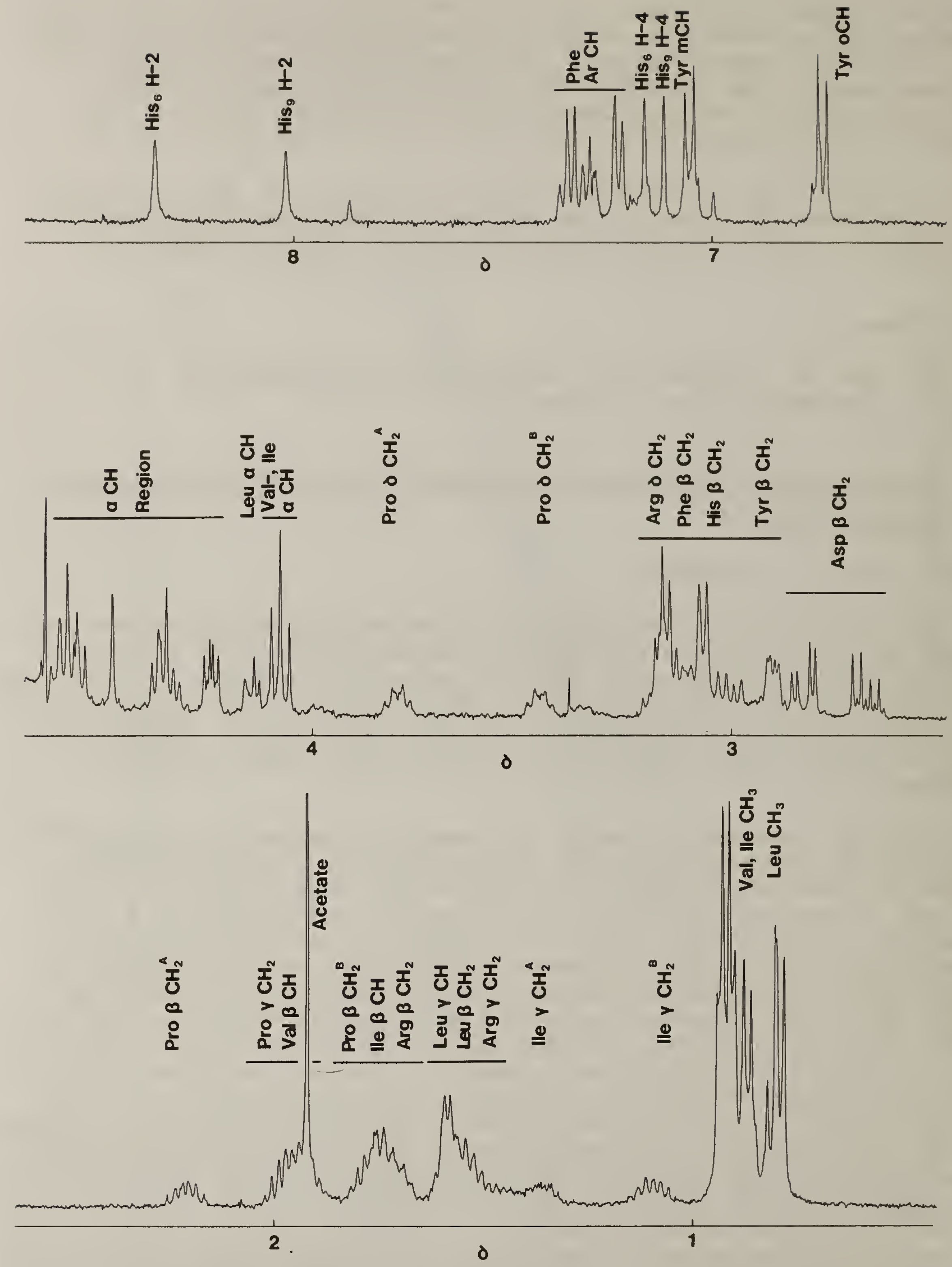

Figure 36. Proton NMR spectrum of angiotensin I at 400 MHz in 100% D_2O. The peptide concentration is 0.5 mg/0.5 mL D_2O. The notations above the peaks indicate the specific proton assignments of each signal or group of signals (indicated by a horizontal line).

Integration of a number of other well-resolved proton multiplets in the NMR spectra of the six samples of Angiotensin I SRM gave information on its amino acid composition (see Table 37). Specific, well-defined proton signals for each amino acid (see figure 36) were identified by use of published spectra and pH induced spectral shifts [1,2], and by comparison of the 400 MHz proton NMR spectra of angiotensin I, II, and valine 5-angiotensin II at acid and neutral pH. The particular signals that were used for quantitation of the amino acids are indicated in Table 37.

Table 37. Analysis of the Amino Acid Content of the Angiotensin I SRM by Proton NMR.

Amino Acid	Proton Signals Used for Quantitation	Relative Amino Acid Content ± S.D. (n=6)
Aspartic acid (Asp)	β-CH_2	1.04 ± 0.04[a]
Histidine 6 (His_6)	H-2 & H-4	0.99 ± 0.05
Histidine 9 (His_9)	H-2 & H-4	0.99 ± 0.03
Isoleucine (Ile)	γ-CH_2	0.98 ± 0.04
Leucine (Leu)	α-CH	0.98 ± 0.04
Leucine + Arginine (Leu + Arg)	γ-CH_2 (of both) and β-CH (leucine)	0.99 ± 0.02
Phenylalanine (Phe)	Phenyl	1.00 ± 0.03
Proline (Pro)	β-CH_2 & δ-CH_2	1.00 ± 0.04
Tyrosine (Tyr)	o and m aromatic	1.03 ± 0.03
Valine + Isoleucine (Val + Ile)	α-CH (both)	1.05 ± 0.02

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[a] Precision expressed as the standard deviation of a single measurement.

The results obtained by this non-destructive technique are in good agreement with those obtained earlier by acid hydrolysis of the SRM followed by high pressure, ion exchange chromatography of the resulting amino acids. The proton NMR results independently confirm the amino acid composition of the SRM and also establish the proline content.

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22. The Synthesis, Purification, and Characterization of 2-Methylthio-oxazoline Derivatives of Pentoses and Hexoses (11320, 51301)

B. Coxon, R. M. Davidson, S. A. Margolis, E. White V

During the past ten years, oxazoline derivatives of carbohydrates have been used as intermediates in the stereospecific synthesis of such anti-tumor nucleosides as 1-β-D-arabinofuranosylcytosine (ara C) and 1-β-D-arabinofuranosyladenine (ara A). In continuation of our investigation of the synthesis and analysis of 2-amino oxazoline derivatives of carbohydrates (see CAC Annual Report, 1981), we have studied the preparation and analytical characterization of a relatively new class of carbohydrate derivatives, the glycosyl 2-methylthio-oxazolines. These derivatives are potentially useful intermediates for the development of efficient nucleoside syntheses that would be completely stereospecific and that would not require the use of anhydrous conditions, exotic catalysts, or protecting groups. Toward these goals, 2-methylthio-oxazoline derivatives have been prepared from D-arabinose, D-lyxose, D-ribose, and D-xylose in the aldopentose series, and from D-allose, D-altrose, D-galactose, and D-glucose in the aldohexose series. The synthetic approach adopted was to convert the free aldoses to 2-thiono-(1,2-dideoxy-D-aldo)[1,2-d]-2-oxazolidine derivatives (some of which were known previously) by treatment with an alkali metal thiocyanate and concentrated hydrochloric acid. The 2-thiono derivatives were then methylated with methyl iodide in the presence of a base catalyst. In principle, such methylations might proceed to give one or more of several products, including those resulting from N-, O-, or S-methylation. However, ^{13}C NMR studies of the products from our optimized methods have indicated that in general, only one methyl group is introduced and its ^{13}C chemical shift is consistent with S-methylation and not with N- or O-methylation.

The types of structures involved are illustrated in figure 37, and the conditions of the methylation reaction were studied initially using 2-thiono derivatives of D-arabinose and D-lyxose, with triethylamine as catalyst. Improved results in terms of the predominance of a single product were obtained when sodium methoxide was used as a catalyst in methanol, at room temperature. A rapid, general procedure has been developed in which the free aldose is converted to the 2-thiono-oxazolidine derivative without isolation of the product, which is then methylated directly in a one-pot reaction. With the ultimate objective of preparing biologically active nucleosides labeled with stable isotopes such as ^{13}C or ^{15}N, 2-methylthio derivatives labeled with these isotopes have also been synthesized from 2-thiono derivatives that were prepared by use of thiocyanate-^{13}C and -^{15}N. The 2-methylthio-oxazoline derivatives have been purified by preparative, reversed-phase HPLC, and characterized by elemental analysis, infrared spectroscopy, and proton and ^{13}C NMR spectroscopy at high field. Mass spectrometry of the products has been initiated.

For the pentosyl 2-methylthio-oxazolines, the type of ring (furanoid or pyranoid) adopted by the pentosyl moiety has been proved by observation of the multiplicities of the H-5, H-5', and hydroxyl signals in proton NMR spectra measured at 400 MHz under hydroxyl proton coupled conditions (DMSO-d_6 solutions). If the structure is pentopyranoid, then H-5 and H-5' do not exhibit coupling to a hydroxyl proton under these conditions, and the hydroxyl proton

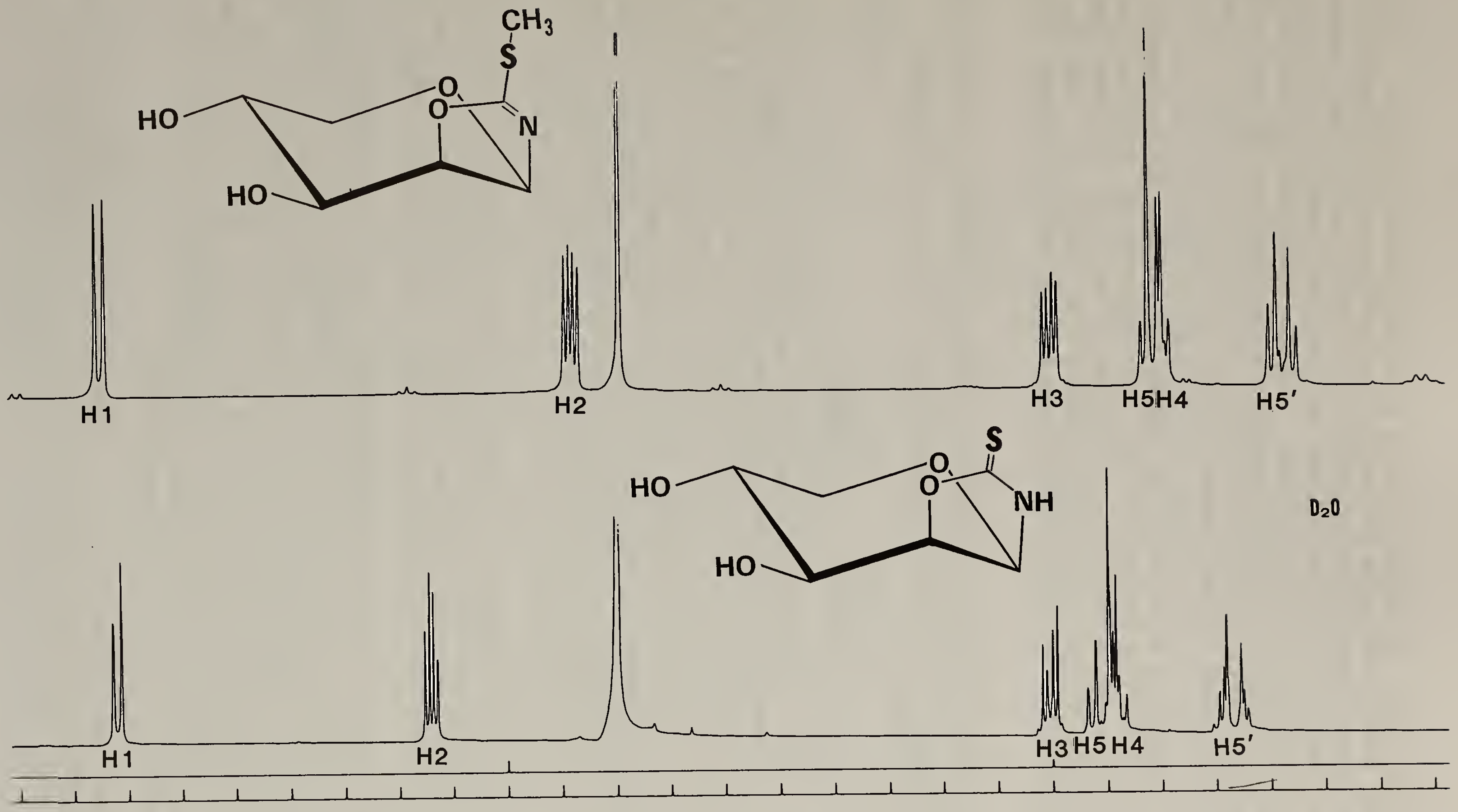

Figure 37. Proton NMR spectra of 2-methylthio-(1,2-dideoxy-β-D-lyxopyrano)[1,2-d]-2-oxazoline and 2-thiono-[1,2-dideoxy-β-D-lyxopyrano)[1,2-d]-2-oxazolidine in D_2O at 400 MHz.

signals each appear as doublets due to coupling with H-3 and H-4. On the other hand, if the structure in question is pentofuranoid, H-5 and H-5' display couplings to HO-5 which itself appears as a triplet, whereas HO-3 resonates as a doublet. Examples of both furanoid and pyranoid 2-methylthio-oxazolines have been found in the pentose series. Similar considerations are being used to define the ring type for the 2-methylthio-oxazoline derivatives in the hexose series, except that it is necessary to determine if H-4 or H-5 is coupled to a vicinal hydroxyl proton.

The assignments for the ^{13}C NMR spectra of the pentose and hexose 2-methylthio-oxazoline derivatives have been confirmed by selective proton decoupling experiments using proton frequencies developed from the specific assignments of the high field proton spectra (see figure 37). Detailed ^{15}N NMR studies of the ^{15}N-labeled derivatives are planned for the near future.

23. An Efficient Two-Step Synthesis of a Novel ^{15}N-Labeled Cyclonucleotide: 2,3'-Anhydro-1-β-D-fructofuranosyluracil-$^{15}N_2$-1',6'-diphosphate

(11320, 51301)

B. Coxon, R. M. Davidson, S. A. Margolis

The utility of carbohydrate oxazoline derivatives as intermediates in the synthesis of potential anti-tumor nucleosides and nucleotides has been tested by condensation of an oxazoline derivative of fructose diphosphate with methyl propynoate. In 1970, Sanchez and Orgel [1] reported a one-step synthesis of α-cytidylic acid from D-ribose-5-phosphate under potentially prebiotic conditions. Therefore, because D-fructose-1,6-diphosphate is an inexpensive commercially available starting material and is stereochemically related to arabinose and psicose (and hence to ara A and ara C), we envisioned a convenient two-step synthesis of a nucleotide that could also be used to generate products labeled with stable isotopes such as carbon-13 and nitrogen-15.

Labeling with nitrogen-15 increases the ease with which ^{15}N NMR spectra can be obtained from small quantities of material, and labeling with carbon-13, or nitrogen-15, or both provides extremely useful materials for the study of tautomeric equilibria, reaction mechanisms, and biochemical degradation.

The reaction of fructose-1,6-diphosphate (FDP) with cyanamide in methanolic solution with guanidine carbonate as catalyst for 24 hours at room temperature yielded a new oxazoline derivative, namely 2-amino-(2,3-dideoxy-β-D-fructofurano)[2,3d]-2-oxazoline-1',6'-diphosphate (FDP-Oxazoline). Unlabeled and ^{13}C and ^{15}N labeled versions of this derivative have been purified by HPLC and characterized by proton and ^{15}N NMR at high field. The ^{15}N NMR spectra of solutions of FDP-oxazoline-$^{15}N_2$ in deuterium oxide have been found to develop additional ^{15}N resonances over the course of 24 hours. The nature of this process is to be investigated further.

Condensation of the FDP-oxazoline with methyl propynoate in saturated aqueous ammonium hydrogen carbonate at 90 °C for 0.5 hour yielded 2,3'-anhydro-1-β-D-fructofuranosyluracil-1',6'-diphosphate (FDP cyclo U, see reaction scheme). This cyclonucleotide is a fructose diphosphate analogue of cyclouridine (cyclo U). After purification by HPLC, the FDP cyclo U was characterized by ultraviolet absorption and proton and ^{15}N NMR spectroscopy. Its UV absorption spectrum is extremely similar to that of cyclo U (λ max 223 and 246 nm *vs.* 222 and 249 nm). The vinyl region in the 400 MHz proton NMR spectrum of FDP cyclo U-$^{15}\underline{N}_2$ is very similar to that of cyclo U-$^{15}\underline{N}_2$ (see figure 38). The aliphatic region of the proton spectra (see figure 39) of FDP cyclo U and its $^{15}\underline{N}_2$ labeled analog show a multiplicity of heteronuclear coupling information. ^{13}C and ^{31}P NMR studies remain to be done.

Reference

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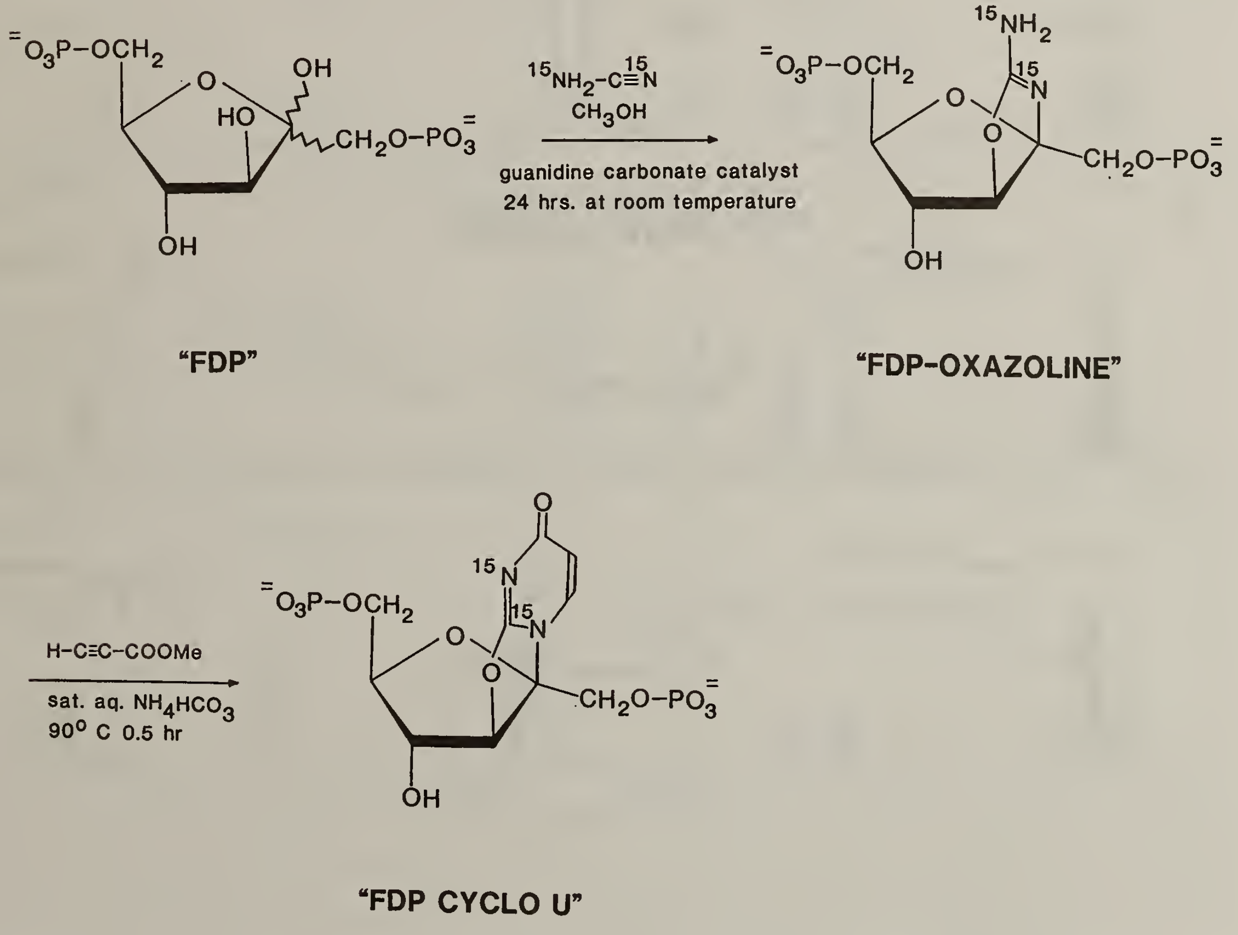

Scheme 1. Scheme for the synthesis of 1-β-*D*-fructofuranosyluracil-$^{15}N_2$-1',6'-diphosphate (FDP cyclo U-$^{15}N_2$) from fructose-1',6'-diphosphate (FDP).

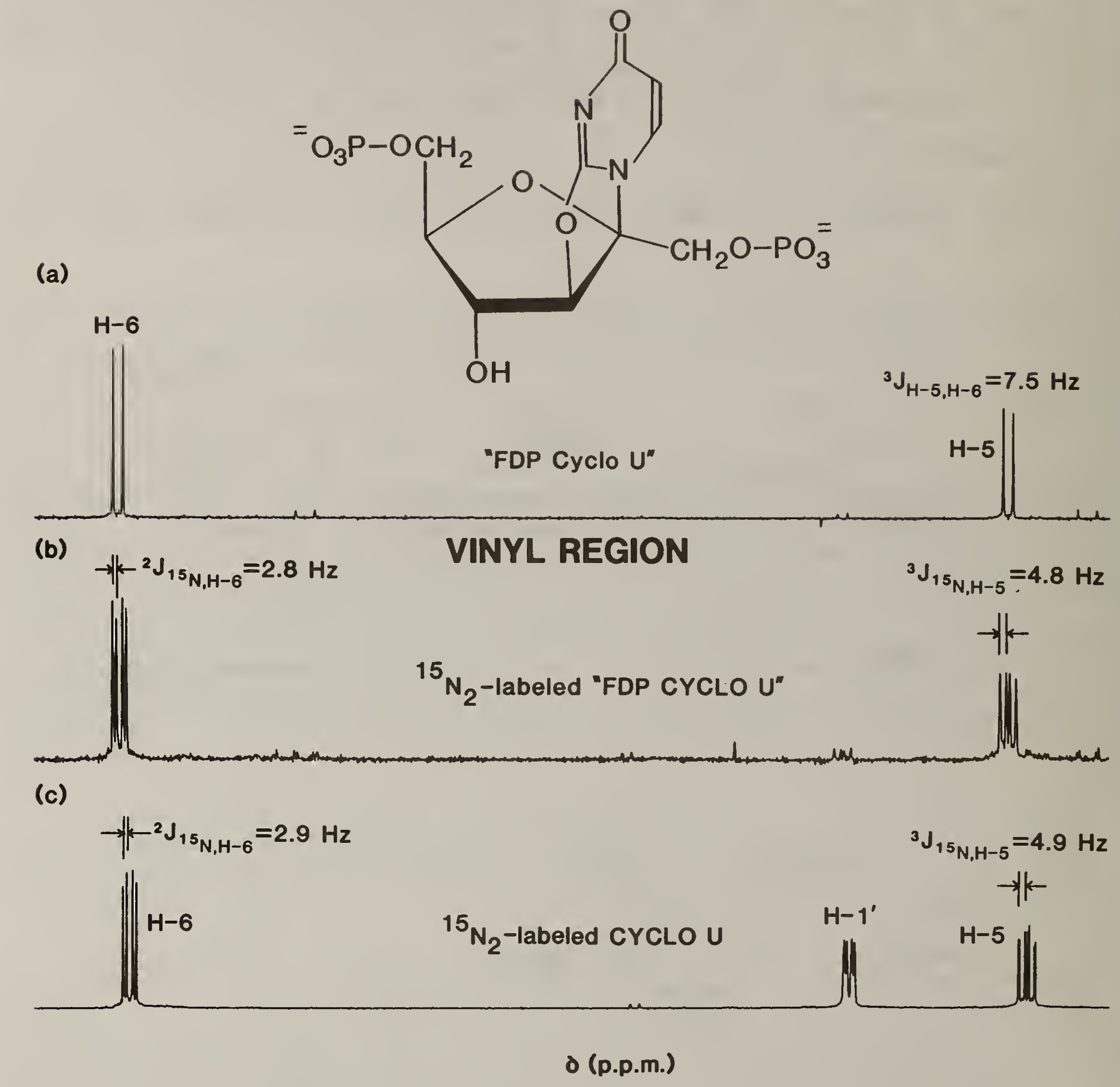

Figure 38. Vinyl regions of the proton NMR spectra (at 400 MHz) of solutions of cyclouridine-$^{15}N_2$(cyclo U-$^{15}N_2$),2,3'-anhydro-1-β-D-fructofuranosyluracil-$^{15}N_2$-1',6'-diphosphate (FDP cyclo U-$^{15}N_2$) and FDP (cyclo U) in D_2O.

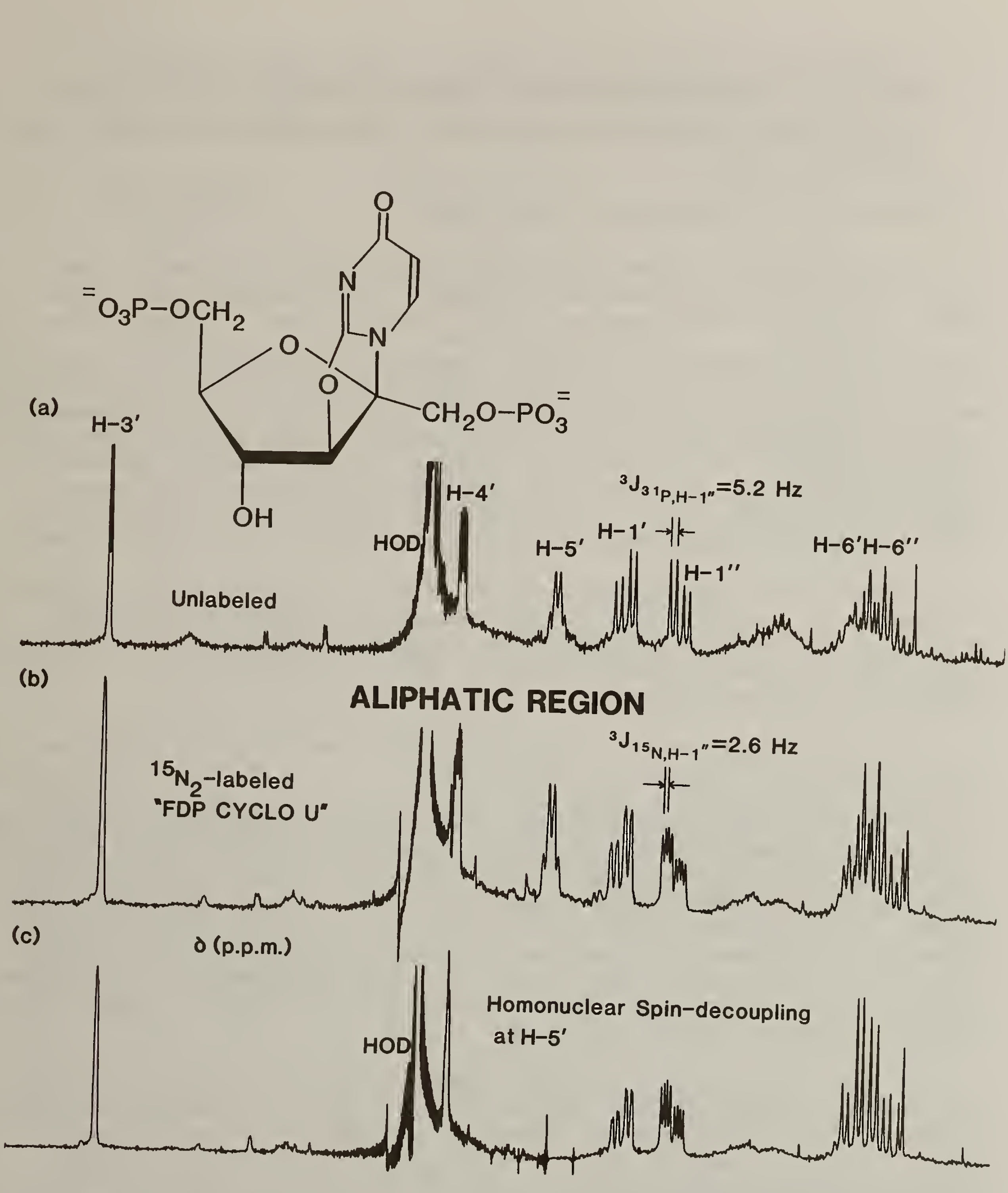

Figure 39. Aliphatic regions of the proton NMR spectra (at 400 MHz) of 2,3'-anhydro-1-β-D-fructofuranosyluracil-1',6'-diphosphate (FDP cyclo U) and FDP cyclo U-$^{15}N_2$, with and without homonuclear spin decoupling of H-5.

24. Confirmation of the Standard Wavelength for the 100 °S Point of the International Sugar Scale by Polarimetric Measurements with a Dye Laser (11320)

B. Coxon, D. K. Hancock, H. Layer (523)

The 100 °S point of the International Sugar Scale is defined as the optical rotation of the normal sugar solution [1] at the wavelength of the green line of the mercury isotope ^{198}Hg(λ_{vac}=546.2271 nm). As part of our contribution to international efforts in establishing a revised 100 °S point value, it was decided that the effective wavelength of the Philips low pressure mercury lamp which was used as a light source in the 100 °S point measurements should be compared with that of the ^{198}Hg isotope. Since optical rotation is directly related to the frequency of the source, this comparison was made by measuring the optical rotation of an internationally measured long quartz rotator, PTB #2, both with a single frequency dye laser locked to the green ^{198}Hg line and with the commonly used Philips mercury lamp as light sources.

Optical rotation determinations made at NBS in 1978 indicated a rotation discrepancy for a quartz control plate between measurements made with the Philips mercury lamp and those made with a dye laser locked to the center of a Doppler-broadened mercury emission from a hollow cathode lamp. This finding necessitated further measurements.

Our present measurements utilized a recently developed system [2] for locking the single frequency dye laser to the 7s ^{3}S, to 6p $^3P_2$ transition of a mercury isotope by means of saturated absorption in a high vacuum quartz cell excited by a radiofrequency discharge. This technique represents a significant increase in accuracy over previous measurements (which used a hollow cathode tube) for two important reasons. Firstly, in previous measurements, the dye laser was locked to the Doppler-broadened profile of a lamp containing natural mercury, the output of which includes emissions from four mercury isotopes. Secondly, in the commercial lamp that was used, the electrical discharge was sustained by a neon buffer gas, so that the average wavelength of the emission from this lamp can vary significantly as the operating conditions, the neon pressure, and the discharge current are varied.

In the present measurements, saturated absorption was used to lock the dye laser to the Lamb dip of either the ^{202}Hg or the ^{198}Hg isotopes which were excited by radiofrequency energy instead of by a direct current discharge. To accomplish this, a special tube was constructed and was filled with highly purified mercury; no buffer gas was used. An optical interference filter was used to prevent spurious emissions from the dye laser from entering the polarimeter. This system has increased the resolution of the wavelength determination by a factor of 300 relative to the system which utilized a hollow cathode tube.

Table 38 compares ratios ($R = [\alpha_\lambda]/[\alpha_{HeNe}]$) of optical rotations measured on quartz plate PTB #2 with various light sources of wavelength λ and with the helium-neon laser.

Table 38. Optical Rotation Ratios (R)[a] for Quartz Plate PTB #2 and Wavelengths (λ) Calculated Therefrom.

Light Source	Optical Rotation Ratios (R)[a]	Wavelength (λ, nm) Calculated from Dispersion Equation[b]
^{202}Hg[c]	1.36629145	546.2278
	1.36629170	546.2278
	1.36628886	546.2283
^{198}Hg[d]	1.36627892	546.2302
	1.36627678	546.2306
	1.36627678	546.2306
Hg lamp	1.3662712	546.2317
	1.3662764	546.2306
	1.3662760	546.2307
	1.3662752	546.2309
	1.3662676	546.2323
	1.3662802	546.2299

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[a] $R = [\alpha_\lambda]/[\alpha_{HeNe}]$.

[b] $\lambda = 0.07360154 + 0.571645053\ (R + 0.03957273)^{-0.558379782}$.

[c] Dye laser locked to ^{202}Hg isotope.

[d] Dye laser locked to ^{198}Hg isotope.

Also in Table 38 are wavelengths λ that have been calculated from an explicit form of the quartz dispersion equation, which was derived by fitting NBS data for PTB #2, PTB #3, and data of the Physikalisch-Technische Bundesanstalt (PTB). Comparison of the calculated effective wavelength of the Philips lamp and the dye laser locked to the ^{198}Hg isotope shows excellent agreement, indicating that no wavelength correction need be made to the 100 °S point data. This work cleared the way for consideration of a revised 100 °S point value at the 18th Session of the International Commission for Uniform Methods of Sugar Analysis (ICUMSA) in June of this year. However, as a result of this meeting, all recommendations pertaining to the new scale have been deferred until the economic and legislative aspects of it can be considered. Because of effects on trade, the implementation of restandardizing quartz plates will not now be decided until the 1986 meeting of ICUMSA at the earliest.

This work also suggests the feasibility of using the NBS high precision polarimeter with a long quartz rotator as a wavelength measuring device. Deviations of our calculated wavelengths from the theoretically determined wavelengths for the 7s ^3S, to 6p $^3P_2$ transition of the mercury isotopes appear to result from the fit of the composite dispersion equation used. Given sufficient data for a single long quartz rotator, it should be possible to derive an individual dispersion equation that would allow one to determine an accurate emission wavelength by means of a simple optical rotation measurement.

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[1] "The 'normal sugar solution' is defined as 26.0160 g of pure sucrose weighed *in vacuo* and dissolved in pure water at 20.00 °C to 100.000 cm^3. This corresponds to a concentration of 26.0000 g of sucrose weighed with brass weights in air under normal conditions (1013 mbar pressure, 20 °C, 50% relative humidity in 100.000 cm^3 of solution at 20.00 °C)." (Officially adopted at the 13th Session of ICUMSA, 1962.)

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25. Implementation of and Initial Research in Two-Dimensional Electrophoresis for Protein Separations (11320, 51111)

D. K. Hancock, D. J. Reeder

Separation and characterization of proteins for eventual use as analytical reagents was implemented with competence building funding. Since this is a new area of research at NBS, an extensive literature search was conducted and reprints were obtained. References and titles were entered into a microcomputer data base for rapid access. At a meeting on two-dimensional electrophoresis (2-DE) held at the Mayo Clinic, contacts were made with many research users of this technique. Laboratory equipment to perform 2-DE was set up and methods were examined for generating gradient polyacrylamide gels, for handling thin (0.7 mm) gels, for staining, and for photographing gels. Isoelectric focusing in long (170 mm) tube gels was implemented using ampholytes from several manufacturers.

To perform studies on the role of materials purity on separations in the 2-DE system, we began initial investigations with sodium docecyl sulfate (SDS), a detergent used extensively in the 2-DE separations. The relative composition of SDS obtained from ten different manufacturers' lots was examined by gas chromatography after hydrolyzing the sulfate esters to free the long-chain (C_{10}, C_{12}, C_{14}) alcohols. The gas chromatograms revealed a wide range of differences in purity of the SDS, with varying ratios of C_{12} to C_{10} or C_{14}. The SDS from each of the ten lots was subsequently incorporated into the sample buffer and running buffer for one-dimensional separations and comparison of banding patterns of six different serum proteins. Correlation of the serum protein banding patterns versus SDS composition is in process.

A modest joint research effort using electrophoresis was started with the Sandy Hook Marine Laboratory, NOAA, Department of Commerce, to investigate electrophoretic protein patterns of different species of flounder. Initially, we ran serum protein patterns for summer, winter, yellowtail, and windowpane flounder to ascertain species interrelationhips and identify similar proteins. Serum was separated by gel filtration chromatography as well as by affinity chromatography and fractions were analyzed by electrophoresis and immunoelectrophoresis. Antiserum for performing immunoelectrophoresis (IEP) was provided by the National Fish Health Research Laboratories, Department of the Interior. Stained IEP slides are now being prepared for photography and for comparison of interrelationships.

Future studies will continue to be centered on the role of materials in the electrophoretic separation process. Studies to determine the mechanism of silver staining are being extended to develop more efficient and sensitive staining procedures. Finally, work will be initiated on modification of proteins for use as stable markers in the 2-DE system.

26. Total Protein Content Certification of SRM 909, Human Serum (14306)

D. J. Reeder

The widespread acceptance of SRM 909, Human Serum, by the clinical community as a standard for inorganic and organic analytes has been enhanced by supplying an information value for the protein content of the reconstituted serum. Because SRM 909 is being used as a standard for many other clinical measurements, requests from many clinical laboratories have been received by the Office of Standard Reference Materials for a protein value on the human serum reference material. Serum protein measurements are a routine clinical measurement, with laboratories often using bovine serum albumin (SRM 927) as a protein standard. Total protein measurements of serum, cerebrospinal fluid, and urine give physicians information concerning a patient's state of hydration, nutrition, and renal condition, as well as revealing potential tumors of bone marrow.

Measurements leading to certification of the protein value were made by using the biuret method for protein developed by Doumas, et al. [1]. Bovine Serum Albumin, SRM 927, was used as the protein standard. We performed the biuret measurements by analyzing ten vials of SRM 909 and ten vials of SRM 927 on two successive days with freshly made reagents each day and reading the absorbance on two separate spectrophotometers. Preliminary calculations result in a value of 63.3 ± 0.3 mg/mL (1 σ). More complete statistical analysis of all of the parameters, using several modeling approaches, is underway.

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27. Construction of a Toxic Chemicals Handling Laboratory (11397)

S. N. Chesler, H. S. Hertz

During 1981 an NBS design concept for a toxic organic chemicals handling laboratory was realized, in terms of a detailed plan prepared by an architectural and engineering consultant. Based upon this plan, construction of a toxic chemicals handling laboratory began in March 1982. The facility is now essentially complete, and we anticipate bringing it into operation during the last few months of 1982.

The laboratory is designed for air to flow over the investigator, then over the work area, and finally through a filter before being exhausted or recirculated. Air is circulated through the laboratory at 8000 cubic feet per minute (CFM) and exhausted through the hoods and toxic chemicals storage cabinets at 1400 CFM. These air flows result in laboratory air being changed every 24 seconds and totally exhausted every 2.3 minutes. The volume and direction of air flows dilute any airborne contamination and direct it away from the laboratory personnel and into charcoal filters for removal. Filtered air and fresh air enter the laboratory through HEPA filters designed to remove any particulate material which might be present.

Toxic chemicals are stored in cabinets which are continuously exhausted and purged with 400 CFM of room air. The direction of air flow again assures that air passes over laboratory workers, then chemicals, and finally through a charcoal exhaust filter when the cabinet is opened.

Two Class II, Type II safety hoods are located in the center of the laboratory. These hoods will be the sole location for transferring and weighing operations requiring the handling of pure liquid and crystalline toxic materials.

We are currently writing a detailed protocol for use of the laboratory. This protocol will include proper procedures for entering and exiting the laboratory, for the use of the laboratory, for comprehensive recordkeeping, for handling emergency situations, for proper disposal of wastes, and for maintaining and cleaning the facility.

C. Outputs and Interactions
(Organic Analytical Research Division)

1. Publications

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Wise, S. A., Analytical Techniques for the Determination of Petroleum Hydrocarbons and Combustion Products, in Pollution and the Protection of Water Quality, Hemisphere Publishing, New York, in press.

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Davidson, R. M., Margolis, S. A., White V, E., Coxon, B., and Oppenheimer, N. J., A New, Facile Synthesis of Pento- and Hexo-Furanosyl 2"-Amino Oxazoline Derivatives, *Carbohyd. Res.*, submitted for publication.

Fatiadi, A. J., Permanganate Ion: An Old, But Still Novel Oxidant in Organic Chemistry, *Oxidate Procedures Involving Metal Compounds in Org. Chem.*, submitted for publication.

Margolis, S. A. and Konash, P. L., The HPLC Analysis of Diastereomers and Structural Analogs of Angiotensins I and II, *Anal. Biochem.*, submitted for publication.

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, submitted for publication.

May, W. E., Miller, M. M., Tewari, Y. B., Brown-Thomas, J. M., and Goldberg, R., The Solution Thermodynamics of Some Slightly Soluble Hydrocarbons in Water, *J. Chem. Eng. Data*, submitted for publication.

Roberts, G. D. and White V, E., Silver Sulfonates as Mass Standards in Field Desorption Mass Spectrometry, *Anal. Chem.*, submitted for publication.

Sniegoski, L. T. and White V, E., Synthesis of 1-Dodecyl-d$_{25}$ Phosphate, *J. Labeled Compounds and Radiopharm.*, submitted for publication.

Sonnefeld, W. J., Zoller, W. H., and May, W. E., A Dynamic Coupled-Column Liquid Chromatographic Method for Determination of Vapor Pressures of Organic Compounds, *Anal. Chem.*, submitted for publication.

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Yap, W. T., Schaffer, R., Hertz, H. S., White V, E., and Welch, M. J., On the Difference Between Linear and NonLinear Models in Bracketing Procedures in Isotope Dilution/Mass Spectrometry, *Biomed. Mass Spectrom.*, submitted for publication.

2. Talks

S. A. Wise, "Research in the NBS Environmental Specimen Bank Relating to Human Nutrition," Holiday Inn City Line, Philadelphia, PA, October 20, 1981. Invited

S. A. Wise, "Analytical Methods for the Determination of Polycyclic Aromatic Compounds on Air Particulate Matter," Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH, October 29, 1981.

W. E. May, "Verification of Analytical Results Through Use of Several Independent Techniques for Quantitation," Chemical Characterization of Hazardous Substances in Synfuels Workshop, Battelle Pacific Northwest Laboratory, Richland, WA, November 6, 1981. Invited

R. A. Durst, "Organic Electrochemical Research at the National Bureau of Standards," Chemistry Department, University of Pittsburgh, Pittsburgh, PA, November 19, 1981. Invited

S. A. Wise, "Characterization of Polycyclic Aromatic Hydrocarbons in Urban Particulate Matter," Aerosol/Small Particle Seminar, National Bureau of Standards, Gaithersburg, MD, November 20, 1981. Invited

W. E. May, "Analytical Methods and Standards for the Determination of PAH in Environmental Samples," Second International Congress on Analytical Techniques in Environmental Chemistry, Barcelona, Spain, November 27, 1981.

B. Coxon, "NMR Spectroscopy at 400 MHz," National Institutes of Health, Bethesda, MD, December 9, 1981. Invited

W. E. May, "Use of HPLC in the Determination of Potentially Toxic Compounds in Alternate Fuels," Chemistry Department, Alabama A&M University, Huntsville, AL, December 10, 1981.

H. S. Hertz, "Analytical Chemical Capabilities of the National Bureau of Standards," Pittsburgh Energy Technology Center, Pittsburgh, PA, December 16, 1981. Invited

R. A. Durst, "Reference Electrodes and Standards for Biomedical Measurements," Symposium on Electrochemical Sensors in Medicine and Medical Research, Park City, UT, January 11, 1982. Invited

H. S. Hertz, "Clinical Chemistry and Related Programs at the National Bureau of Standards," Veterans Administration, Washington, DC, February 8, 1982. Invited

H. S. Hertz, "Quantitative Trace Organic Analysis," Aberdeen Proving Grounds, Edgewood, MD, March 10, 1982. Invited

D. K. Hancock, "Inorganic Ion-Doped Glass Beads as Microspectrofluorimetric Standards," 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 10, 1982.

K. A. Bunding, "The Surface-Enhanced Raman Spectroscopy of N-Methylpyridinium Ion on a Silver Electrode," American Physical Society Meeting, Dallas, TX, March 11, 1982.

H. S. Hertz, "Measurement of Trace Organic Pollutants in Water," 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 11, 1982. Invited

W. J. Sonnefeld, "On-Line Multidimensional High-Performance Liquid Chromatography Coupling Normal- and Reversed-Phase Systems," 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 11, 1982.

A. J. Fatiadi, "The Hillebrand Award Address: Chemistry of Oxocarbons and Pseudo-Oxocarbons. New Organic Semiconductors," The Chemical Society of Washington, Knights of Columbus, Arlington, VA, March 11, 1982.

W. F. Kline, "Chromatographic Methods for the Determination of Valproic Acid and Carbamazepine in Freeze-Dried Human Serum," 1982 Pittsburgh Conference on Alalytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 12, 1982.

H. S. Hertz, "Research in Isotope Dilution Mass Spectrometry and Combined Liquid Chromatography/Mass Spectrometry for Clinical Analysis," Johns Hopkins University, Baltimore, MD, March 12, 1982. Invited

B. Coxon, "NMR Spectroscopy of Carbohydrates at 400 MHz," School of Medicine, Johns Hopkins University, Baltimore, MD, March 19, 1982. Invited

R. M. Davidson, "An Efficient Two-Step Synthesis of a Novel ^{15}N-Labeled Cyclonucleotide: 2,3'-Anhydro-1-β-D-Fructofuranosyluracil-$^{15}N_2$-1',6'-Diphosphate," American Chemical Society Meeting, Las Vegas, NV, April 2, 1982.

R. M. Parris, "Analysis of Polychlorinated Biphenyls in Waste and Lubricating Oils," Student Seminar, University of Maryland, College Park, MD, April 12, 1982.

B. Coxon, "NMR Spectroscopy at High Field," Chemistry Department, University of Maryland, College Park, MD, April 13, 1982. Invited

L. R. Hilpert, "Analyses of Aqueous Leachates of SRC II Vacuum Still Bottoms," Review Meeting on Hazardous Wastes, Pittsburgh Energy Technology Center, Pittsburgh, PA, April 14, 1982.

E. A. Blubaugh, "Organic Electrochemical Techniques of Potential Clinical Application," Symposium on Advanced Analytical Concepts for the Clinical Laboratory, Riverside Motor Lodge, Gatlinburg, TN, April 30, 1982.

R. G. Christensen, "Quantitative Trace Analysis by Reversed-Phase LC/MS," Society for Applied Spectroscopy Meeting, Ramada Inn, Chicago, IL, May 4, 1982. Invited

S. A. Wise, "Operation of the U.S. Pilot National Environmental Specimen Bank Program," International Workshop on Environmental Specimen Banking and Monitoring as Related to Banking, University of Saarland, Saarbrücken, Germany, May 9, 1982.

R. Schaffer, "Definitive Methods for Organic Analytes for Clinical Chemistry," Fourth International Symposium on Quantitative Mass Spectrometry in Life Sciences, Ghent, Belgium, May 13, 1982. Invited

S. A. Wise, "Analytical Techniques for Organic Analysis of Environmental Samples," Seventh Annual U.S./German Seminar of State and Planning for Specimen Banking, Munich, Germany, May 17, 1982. Invited

S. A. Wise, "Experimental Design for Collection and Storage of Mussels," Seventh Annual U.S./German Seminar of State and Planning for Specimen Banking, Munich, Germany, May 18, 1982, with K. Kafadar. Invited

L. R. Hilpert, "Quantitative Analysis of Individual Organic Compounds in an SRC II Coal Liquid," U.S. Department of Energy, Sixth Annual Meeting on the Characterization of Coal-Derived Material, Ramada Inn, Pittsburgh, PA, May 20, 1982. Invited

W. J. Sonnefeld, "Multidimensional HPLC Techniques Applied to the Determination of Polycyclic Aromatic Compounds in Complex Mixtures," Sixth International Symposium on Column Liquid Chromatography, Cherry Hill Inn, Cherry Hill, NJ, June 7, 1982.

S. A. Wise, "The Effect of C_{18} Surface Coverage on Selectivity in Reversed-Phase Liquid Chromatography of Polycyclic Aromatic Hydrocarbons," Sixth International Symposium on Column Liquid Chromatography, Cherry Hill Inn, Cherry Hill, NJ, June 7, 1982.

L. T. Sniegoski, "Synthesis and Use of Isotopically Labeled Materials in the Development of Reference Materials at the National Bureau of Standards," International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds, Kansas City, MO, June 8, 1982.

E. White V, "Quantitative Trace Analysis by Reversed-Phase LC/MS Employing Continuous Sample Preconcentration," American Society for Mass Spectrometry Meeting, Hilton-Hawaiian Village, Honolulu, HI, June 10, 1982.

L. R. Hilpert and K. L. Richie, "Mass Spectrometric Determination of Trace Organic Compounds in Aqueous Wastes Associated with Energy Production," American Society for Mass Spectrometry Meeting, Hilton-Hawaiian Village, Honolulu, HI, June 11, 1982.

W. E. May, "Multidimensional HPLC Analysis Applied to the Determination of PAH and Related Compounds in Complex Mixtures," Ohio Valley Chromatography Forum, Hyeston Woods State Park Lodge, Oxford, OH, June 18, 1982.

K. A. Bunding, "Surface-Enhanced Raman Investigations of Surface Species: N-Methylpyridinium and Pyridine Competition," International Conference on Electronic and Molecular Structure of Electrode-Electrolyte Interfaces, Eccles Conference Center, Utah State University, Logan, UT, July 29, 1982.

R. A. Durst, "Surface-Enhanced Raman Spectroscopy of N-Methylpyridinium Cation and Pyridine: Identification of Surface Species," International Conference on Electronic and Molecular Structure of Electrode-Electrolyte Interfaces, Eccles Conference Center, Utah State University, Logan, UT, July 29, 1982.

H. S. Hertz, "Results of Interlaboratory Quantification of Organics in Fossil Energy Leachates," Laramie Energy Technology Center, Laramie, WY, August 3, 1982. Invited

D. J. Reeder, "Certification Methods for SRM 1599: A New Anticonvulsant Drug Standard," Anaheim, CA, August 9, 1982.

B. Coxon, "Nitrogen-15 NMR Spectroscopy of Aminoglycosides," Eleventh International Carbohydrate Symposium, University of British Columbia, Vancouver, British Columbia, Canada, August 23, 1982.

M. L. Fultz, "An Electrochemical and Spectroelectrochemical Study of Copper Bleomycin and Iron Bleomycin," 1982 Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 20, 1982.

W. E. May, "Liquid Chromatographic Methods for the Determination of Polycyclic Aromatic Hydrocarbons in Air Particulate Extracts," 1982 Fall American Chemical Society Meeting, Kansas City, MO.

W. E. May, "First-Line Supervision of an Analytical Research Group," 1982 Fall American Chemical Society Meeting, Kansas City, MO.

3. Committee Assignments

Harry S. Hertz
- Chairman, ASMS, Committee on Education
- 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
- Board of Directors, NCCLS
- Technical Advisor, OIML, SP26, Subcommittee Sr5 on Reference Materials for Calibration of Instruments Meant for Checking Substances During Medico-Biological and Research Analyses

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

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
- Secretary, IFCC, Scientific Committee, Analytical Section, Expert Panel on pH and Blood Gases
- 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
- Consultant on Electrochemistry, U.S. Army, Task Group on Medical Bioengineering R&D Laboratory

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

Dennis J. Reeder
- Member, AACC
  - Study Group on Cortisol
  - Study Group on Total Serum Protein
- Associate Member, IFCC, Expert Panel on Drug Effects in Clinical Chemistry
- Chairman, NCCLS, Subcommittee on Specific Plasma Proteins
- 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 2, 1981 - Olmes Bisi, University of Modena, "Transitional Metal Silicides: Their Chemical Bonds and Electronic Structure".

October 16, 1981 - Dennis J. Reeder, National Bureau of Standards, "Proteins in Analytical Chemistry".

October 19, 1981 - Kathryn A. Bunding, National Bureau of Standards, "Surface-Enhanced Raman Spectroscopy Experiments With Substituted Pyridines and Their Theoretical Implications".

October 22, 1981 - Charles H. Lochmuller, Duke University, "The Role of Chemically Modified Surfaces in Chromatographic Resolution".

February 19, 1982 - James I. Garrels, Cold Spring Harbor Laboratory, "Two-Dimensional Electrophoresis: From Specialized Laboratory to Data Management".

March 3, 1982 - Alexander J. Fatiadi, National Bureau of Standards, "Chemistry of Oxocarbons and Psuedo-Oxocarbons: New Organic Semiconductors".

March 22, 1982 - Robert M. Davidson, National Bureau of Standards, "An Efficient Two-Step Synthesis of a Novel ^{15}N-Labeled Cyclonucleotide: 2,3'-Anhydro-1-β-D-Fructofuranosyluracil-^{15}N$_2$-1',6'-Diphosphate".

May 4, 1982 - Elena Katz, Perkin-Elmer Corporation, "The Use of Small Particles in High-Speed Liquid Chromatography".

May 6, 1982 - Dennis Schuetzle, Ford Motor Company, "Identification of Nitrated Polynuclear Aromatic Hydrocarbons in the Environment".

July 15, 1982 - Richard Laub, Ohio State University, "How to Separate Almost Anything from Practically Everything Else".

August 5, 1982 - Georges Guiochon, Laboratoire de Chimie Analytique Physique, France, "Bidimensional Chromatographic Analysis".

August 13, 1982 - Bruno Pettinger, Fritz Haber Institute der Max Planck Gesellschaft, Berlin, West Germany, "Influence of Foreign Metal Atoms Deposited at Electrodes on Local and Non-Local Processes in SERS".

b. Conferences Sponsored

October 18-24, 1981 - 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, Washington, DC.

August 25-26, 1982 - W. E. May, The Analysis of PAH in Complex Mixtures, Coordinating Research Council Workshop, National Bureau of Standards, Washington, DC.

c. Seminars Organized

H. S. Hertz, Workshop on the Teaching of Mass Spectrometry, American Society for Mass Spectrometry Annual Meeting, Honolulu, HI, June 7-10, 1982.

d. SRM Certification

1) SRM 909, Human Serum
2) SRM 998, Angiotensin
3) SRM 1514, DTA Purity Set (In Process)
4) SRM 1549, Powdered Skim Milk (In Process)
5) SRM 1581, Polychlorinated Biphenyls in Oil
6) SRM 1582, Petroleum Crude Oil (In Process)
7) SRM 1590, Wine
8) SRM 1595, Tripalmitin
9) SRM 1599, Valproic Acid and Carbamazepine in Human Serum
10) SRM 1639, Drinking Water (In Process)
11) SRM 1647, Priority Pollutant Polynuclear Aromatic Hydrocarbons
12) SRM 1649, Urban Dust/Organics

IV. Gas and Particulate Science Division

Harry L. Rook, Chief
Raymond L. McKenzie, Deputy Chief

A. Division Overview

The Gas and Particulate Science Division performs research on new and improved techniques for the measurement of chemical composition on a microscopic scale and conducts research on measurement methods for gaseous molecules in controlled mixtures and at trace atmospheric levels. The results of this research are applied to NBS and other international standards programs and, in selected areas, applied to high priority national problems as addressed by other federal agencies and private industry. The Division's programs are carried out by four groups with scientific effort divided approximately equally between gas analytical research and microanalytical research.

During the past year, substantial progress has been made on the Compositional Mapping competence building program. Research on the new ion microscope has been directed toward quantitative two dimensional mapping of chemical features on an x,y planar sample. To aid this type of analysis, a DeAnza image array processor is being interfaced between a special television output of the ion microscope signal and the Division DEC VAX computer. This system, when complete, will directly acquire ion images in digital form from the channel plate detector of the ion microscope and allow automated image processing of chemical and isotopic data. The speed and memory capacity of the VAX will allow direct transformation of the large data arrays obtained in two and three dimensional compositional mapping and will allow construction of three dimensional compositional images. A second accomplishment in this program has been the intercomparision of depth profile information derived independently by neutron and ion depth profiling techniques. The results of that joint study were recently reported at the annual Microbeam Analysis Society Meeting in Washington, DC. Other accomplishments in microanalysis research include the final measurement and certification of the first Asbestos SRM; the development of accurate isotopic measurements using laser microprobe mass analysis (LAMMA) on sample sizes as small as a few femtograms of total material; research leading to chemical and isotopic characterization of individual submicrometer particles; and finally, the development of a method for sequential instrument analyses of single particles by AEM and LAMMA.

In the area of atmospheric and gas measurement research, major achievements include the development of a multicomponent atmospheric standard co-certified for CO_2 and N_2O concentrations with information on the F-11 and F-12 concentrations; the development of an optoacoustic technique for the measurement of the gaseous HCl molecule with a potential sensitivity below 0.1 ppm by volume; successful measurements of the carbon-14 content of samples as small as 100 μg total mass by Accelerator Mass Spectrometry; the accurate preparation and analysis of ppb level multicomponent organic constituents in air-gas mixtures; and finally, the completion of CRM traceability protocols for SRM containing NO, SO_2 and propane.

As in the past, the Division has been a major contributor to the NBS SRM program both in research leading to new and better standards as well as in the certification of current SRM's. Over 2600 individual samples of more than 65 different SRM's have been analyzed for certification during the year.

Future directions in microanalysis research will continue to focus on quantitative compositional mapping and the development of quantitative analytical methods for the ion microscope and the LAMMA. This research will include: multidimensional chemical and isotopic mapping; automated imaging of chemical maps; multiparameter analysis using two or more microanalytical techniques; and the development of computer techniques for data reduction and for the transformation of chemical maps containing large multielement data sets.

Future directions in gas analytical research will build on the recent successes in diode laser photometry and in optoacoustic spectroscopy and the need to develop independent primary measurement methods for many of the simple gaseous molecules presently certified by gravimetry and comparator analysis. Research in the coming year will include: isotope dilution gas mass spectrometry for the accurate analysis of CO_2; the measurement of improved photometric cross sections for use in diode laser IR photometry; research into response mechanisms of electron capture detectors for use in trace gas analysis; and finally a collaborative study of material transport from spark discharges on bulk samples to regions of analytical interest.

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 morphological characterization of matter on the micrometer and sub-micrometer spatial scales. 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, analytical electron microscopy, electron energy loss spectrometry, secondary ion mass spectrometry, laser micro-Raman spectrometry, and laser microprobe mass analysis. Research is conducted on several aspects of each technique, including (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 techniques as a means of disseminating developments; (4) applying results of the research to develop improved compositional mapping techniques; and (5) the study of specific analytical problems in support of NBS and other government agency activities.

A major highlight of FY-82 has been analytical research on the CAMECA IMS-3F ion microscope, an advanced form of secondary ion mass spectrometer. The ion microscope is an imaging mass spectrometer which provides true microscope images of the surface of a sample formed with secondary ions of a particular mass-to-charge ratio. The edge resolution of these images is less than 1 micrometer, and the system is capable of operating with a mass resolution greater than 10,000. The system has been used initially for the study of depth distributions of ion-implanted arsenic in silicon in support of the development of an SRM (in conjunction with the Center for Electronics and Electrical Engineering) and for the study of the participation of oxygen in the phenomenon of diffusion-induced grain boundary migration (in conjunction with the Center for Materials Research). The ion microscope will be a major component in the development of the Compositional Mapping Facility. To implement this facility, a DeAnza image array processor was also acquired during FY-82 and is now being interfaced to the DEC VAX computer and to a special television camera. This system will directly acquire ion images in digital form from the channel plate detector of the ion microscope and allow automated image processing.

During FY-82, the final stages of the production and certification of an Asbestos Counting Material SRM were completed. This project has involved extensive staff effort and has required the development of new techniques of standardization for this unusual standard. This SRM is expected to have a significant impact in standardizing the electron microscope techniques used to determine environmental asbestos exposure.

Further investigations into the analytical capabilities of the laser microprobe mass analyzer (LAMMA) have been carried out to assess the potential of this instrument for trace and isotopic analysis. Limitations to the accuracy and precision of isotopic ratio measurements have been identified. In particular, the performance of the ion detector and the digital transient recorder have been examined. Despite the limitations imposed by these components, useful isotopic measurements were carried out on nanogram quantities of osmium in a joint study with Lawrence Livermore Laboratory to establish the decay rate of rhenium-187.

A major advance in the analysis of sub-micrometer particles was achieved by the development of techniques for sequential analysis of individual sub-micrometer particles by means of an analytical electron microscope (AEM) and laser microprobe mass analysis (LAMMA). Following non-destructive AEM analysis for morphology, major chemical elements, and crystallography, useful mass spectra were obtained with the LAMMA from individual particles as small as 0.1 micrometer in diameter, which is equivalent to a particle mass of approximately 10 femtograms. The combination of morphology, elemental and isotopic analysis, and crystallography provides an extensive characterization of a particle. AEM-LAMMA combined analysis will be a major area of activity in the near future for our Group in cooperation with other Groups in CAC and elsewhere at NBS as we explore the unique capabilities of these complementary techniques.

We have continued our studies of electron interactions in solids in support of electron microprobe and analytical electron microscope measurements. The Monte Carlo simulation technique has been adapted to special sample geometries appropriate to the AEM. In order to simulate more closely electron interactions in the target, the phenomenon of fast secondary electron production has been included in the simulation. This phenomenon appears to be especially important in setting an ultimate limit to the spatial resolution of spectrometries based on inner shell ionization at high beam energies.

During FY-82 we have extended our interactions with other groups at NBS. Microbeam analysis techniques have been utilized in support of (1) the development of neutron beam depth profiling (in conjunction with the Inorganic Analytical Research Division); (2) studies of the phenomenon of diffusion-induced grain boundary migration (in conjunction with the Metallurgy Division); (3) depth distribution of arsenic in silicon (in conjunction with the Center for Electronic and Electrical Engineering); and (4) studies of the microstructure of cement (in conjunction with the Center for Building Technology).

Plans for activities of the Microanalysis Research Group for FY 83/84 are principally centered around research in all of our existing microanalytical methods, and especially into compositional mapping with the ion microscope and extending our understanding of sub-micrometer analysis by means of laser microprobe mass analysis and analytical electron microscopy. To achieve more useful quantitative elemental and isotopic analysis with the LAMMA, considerable improvement must be realized in the detection and signal digitization systems as well as in an understanding of the physical factors which control the ionization process. To implement these LAMMA studies, and to advance the state of quantitative analysis by means of analytical electron microscopy, we plan to work actively in the development of "high technology" standards for sub-micrometer analysis; sputtered glass thin films represent the first venture in this area. Finally, since our past experience has shown that active involvement with applications of microanalysis to high priority problems provides a useful stimulus to research, we anticipate continued collaboration with researchers within NBS, with several universities and with other government agencies.

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Gregory R. Downing, Edgar S. Etz, Inga I. Holl, Ryna B. Marinenko,
Robert L. Myklebust, Patrick J. Sheridan, David S. Simons, John A. Small,
Eric B. Steel, Barbara B. Thorne

2. X-ray Fluorescence Group: Overview

The X-Ray Fluorescence Group performs research on improved techniques for sample preparation and matrix effect calculations to increase the sensitivity and accuracy of x-ray fluorescence spectrometry with respect to the chemical composition of bulk samples.

In FY 82, the X-Ray Spectrometry Group has completed a study on the application of a preconcentration method using cation-exchange resin filters for the analysis of selected elements in NBS-SRM's 1577 Bovine Liver and 1575 Pine Needles. During this work we investigated several sample dissolution methods to improve recoveries of elements such as iron. A research paper on this work has been submitted for publication. Important progress has also been made in the development of an algorithm for the calculation of the spectral output distribution of x-ray tubes. This is an important step in our program towards the development of a comprehensive fundamental parameters method for quantitative x-ray analysis. We plan to continue the development of our fundamental parameter algorithm and to assess the accuracy of interelement corrections calculated from theory when applied to acutal samples. We are also in the process of certifying thin glass films to serve as NBS-SRM x-ray spectrometer standards. A major portion of our work consists of the quantitative analysis and homogeneity testing of renewal SRM's. During this year we have characterized a number of alloy SRM's with our automated wavelength-dispersive spectrometer.

Future directions in x-ray fluorescence research will focus on the continued development of a comprehensive fundamental parameters method for matrix effect calculations. We also plan to evaluate the expected increase in x-ray signal-to-background with a toroidal monochromator especially designed for energy-dispersive x-ray fluorescence analysis.

Peter A. Pella, Group Leader; Anthony A. Marlow, John S. Sieber

3. Atmospheric Chemistry Research Group: Overview

The Atmospheric Chemistry Research Group conducts research on measurement techniques for ambient concentrations of atmospheric species in both the gas and particle (liquid and solid) phases. This research includes the development of both collection and *in situ* analytical methods. A primary objective of this research is the extension of existing techniques and the development of new analytical techniques for the detection and characterization of trace and ultratrace level atmospheric materials.

Several important accomplishments have been achieved in spectroscopic analytical methods. 1) The work on determination of the ozone ultraviolet absorption cross-section values and the temperature dependence of the absorption cross section has continued this year. Detailed measurements of the temperature dependence from 210 to 295 K of the eight principal Dobson bands have improved the accuracy of these coefficients such that the inconsistencies previously encountered in comparing data obtained by various ground-based measurement techniques have been resolved. 2) The design and construction of a new standard reference ozone photometer has been completed and is in the final stage of evaluation and calibration. The photometer, to be used as the calibration standard by the EPA, has an accuracy of 2 percent (limited by the uncertainty of the cross-section value) and a precision of better than 0.3 percent. 3) In a continuation of studies of the measurement of NO_2 by photoacoustic spectroscopy, a detailed characterization of a measurement interference mechanism involving energy transfer from excited NO_2 molecules to O_2, resulting in decreased sensitivity as a function of the oxygen concentration, has been concluded. 4) A second major accomplishment in photoacoustic spectroscopy has been the development of an optoacoustic technique for the measurement of HCl. This technique has an extrapolated sensitivity of 50 ppb by volume and provides the only available *in situ* measurement method for this very important reactive atmospheric gas.

Several major accomplishments have been achieved relating to the measurement and interpretation of radiocarbon concentration and isotope ratios in atmospheric and environmental samples. The application of Accelerator Mass Spectrometry to radiocarbon measurements has resulted in the ability to measure samples as small as 100 μg-carbon with an accuracy of 10 percent. This was achieved through the development of very precise quantitative chemical conversion and transport processes of minute quantities of carbonaceous samples. The continued development of receptor modeling and source apportionment techniques has occured in parallel to the improvements in radiocarbon analysis. This year, advances have occurred in the application of source modeling techniques including insights on experimental design to maximize the accuracy and resolution of source parameters by various analytical techniques.

Gas and particle personnel monitor development and evaluation have continued this year for the EPA. Several NO_2 passive samplers have been investigated under static conditions and in the wind tunnel to evaluate sampling errors that occur due to wind velocity and directional effects. A new sampler for NO_2 was developed that has a sampling rate that makes it compatible with the sampling parameters of the Portable Ambient Aerosol Sampler developed last year. This demonstrates the feasibility of developing a portable sampler capable of providing exposure measurements of both gaseous and inhalable particulate atmospheric materials. The Personal Ambient Aerosol Sampler has been intercompared with stationary samplers this year to validate its performance characteristics against commonly used field methods (the dichotomous sampler). The sampler performed very well and there is an interest by the EPA to incorporate it in field studies they are conducting.

A number of studies have been initiated this year in various aspects of particle characterization. A major component of a Center-wide collaborative study on the transport of material from bulk samples by spark discharge is the characterization of the size and elemental composition of the material sampled and transportable from the sample. Experiments have been designed and initiated to study this process. A collaborative study with members of the Fire Research Division is underway to measure the refractive index of aerosols and smoke particles. The study will be extended to measure the refractive indices of droplets of supersaturated solution formed by evaporation. The supersaturated solutions are stable in sub-micrometer droplets and will provide a way to measure and compare the refractive indices with those of the bulk solution.

Research activities anticipated for the next year include: a) continued development of spectroscopic and optoacoustic measurement techniques of major and trace constituent atmospheric gases; b) application of radiocarbon concentration and isotope ratio measurements to atmospheric hydrocarbon samples; c) continued characterization of the wavelength and temperature dependence of ozone ultraviolet absorption cross-section values; d) application of source and receptor modeling techniques to environmental studies (including possible involvement in an acid-rain study); e) characterization of sampling and transport from bulk materials by spark discharge; f) study of the optical properties of particles and droplets by *in situ* measurements; and g) development of application of the Laser Analytical Microprobe Mass Analyzer for analysis of particulate samples.

Raymond McKenzie, Group Leader; Arnold Bass, Robert Continetti, Lloyd Currie, Robert Fletcher, Alan Fried, Robert Gerlach, Rudy Kelly, George Klouda, David Krask, James Norris, Gerald Tompkins

4. Gas Metrology Group: Overview

The Gas Metrology Group conducts fundamental and applied research leading to the advancement of measurement science and the development of accurate and reliable standards for a variety of gaseous species. These species comprise both inorganic and organic materials that are volatile at room temperature. Basic measurements and research are carried out to assure that the standards that are developed are accurate and stable, as well as to further the scientific understanding of the chemical instability and physicochemical behavior of gaseous species. The Group interacts directly with technical staffs at NBS, universities, other agencies, and industry, as well as with appropriate interagency committees (e.g., Interagency Committees on Carbon Dioxide and Climate, Stratospheric Ozone Protection, Indoor Air Quality) and international bodies (e.g., International Standard Organization and the World Meterological Organization). In addition, a limited gas analysis service, utilizing the unique capabilities of the Group, is provided to other groups at NBS and to other national and international government agencies.

A major accomplishment of the Group this year has been the establishment of primary gas standards for CO_2 in air at atmospheric concentrations which were intercompared with manometric measurements made by Scripps Institute of Oceanography (SIO). This ensures that an effective and logical transfer can be made to NBS from SIO, which has provided CO_2 standards to the World Meterological Organization and NOAA for the past two decades. NBS, hence, will become the focal point for CO_2 standards to quantify measurements of atmospheric CO_2 and has been designated as lead agency for CO_2 atmospheric standards by the Interagency Committee on CO_2 and Climate.

Related to the development of CO_2 standards has been research which is leading towards the co-certification of N_2O and CO_2 at atmospheric concentrations and concentration information on freons F-11 and F-12 in the same standards. Laser-diode and Fourier transform infrared spectroscopy (FTIR) studies have continued on N_2O, F-11, and F-12. Measurements recently completed on the strongest band systems of F-11 and F-12 in an "atmospheric window" by FTIR indicate absorbances 17 percent and 5 percent greater, respectively, than those values used in recent greenhouse warming calculations.

A third component of the Group's gas standards work has been the furtherment of the Certified Reference Materials (CRM's) traceability program which defines protocols by which commercial gas standards manufacturers can develop pollutant gas standards (CRM's) at concentrations that are directly traceable to NBS SRM's. In addition to CO, protocols have now been prepared for NO, SO_2, and propane CRM's. This program is carried out in concert with the Compressed Gas Association and EPA to ease past excessive demands on NBS gas SRM stocks, and to concomitantly ensure that needed reliable gas standards are readily available to industry and national air quality monitoring programs.

In the organic gas standards area, major accomplishments have been the certification of concentrations and stabilities for SRM gas cylinder mixtures containing benzene and tetrachloroethylene, the accurate preparation of ppb-level gravimetric organic gas mixtures, and the accurate preparation of a set of trace level multicomponent organic gas mixtures in nitrogen.

Research on a high-rate passive personal sampler has been completed. The new sampler is capable of providing time-integrated data to quantify personal ambient exposures to NO_2. This sampler design, which is simple and inexpensive, has been characterized and calibrated, and found to provide measureable exposure information in as little as an hour. The sampler is sensitive to below 10 ppb NO_2/hour exposures, and insensitive to humidity or the presence of NO.

Ancillary accomplishments include the preparation and analysis of mixtures of ^{36}Ar and ^{40}Ar and the provision of the mixtures in eight cylinders to NASA. Half of these were sent to the USSR. The mixtures were prepared at the request of NASA for calibrating mass spectrometers and gas chromatographs used in the U.S. Pioneer and USSR Venera missions for analyzing the atmosphere of Venus.

Future research plans of the Gas Metrology Group include: (1) continuing research in laser/FT infrared spectroscopy as an accurate and sensitive analytical technique. (2) research for identification and measurement of gas instability and reaction products using FTIR and mass spectrometry; (3) investigation of electron capture (EC) response mechanisms and characteristics for quantifying low-level EC-sensitive gas species; (4) research on the use of gas chromatography for thermodynamic data; and (5) assessment of candidate "absolute methods" for quantification of gas mixtures.

Walter L. Zielinski, Jr., Group Leader; Barry C. Cadoff, William F. Cuthrell, William D. Dorko, James W. Elkins, Ernest E. Hughes, Patricia A. Johnson, Gerald D. Mitchell, Richard C. Myers, George C. Rhoderick, William P. Schmidt, Gerald A. Sleater, James E. Suddueth.

B. Selected Technical Accomplishments
(Gas and Particulate Science Division)

1. Isotopic Abundance Measurements with the Laser Microprobe Mass Analyzer (11330)

D. S. Simons

The Laser Microprobe Mass Analyzer (LAMMA), which combines a laser ablation ionization source with a time-of-flight mass spectrometer, has proven to be a versatile tool for materials analysis of particles and thin sections. Because a mass spectrometer is used as the detector of the emitted ions, the LAMMA is capable of determining isotopic as well as elemental abundance information. However, only one published study to date has exploited this isotopic capability.

The determination of isotopic abundances in the LAMMA is inherently more precise than the determination of elemental abundances. In the latter case relative ionization efficiencies among elements can be strongly affected by the details of the laser-solid interaction, in analogy with the well-known matrix effects that arise from the ion-solid interaction in secondary ion mass spectrometry (SIMS). Matrix effects are usually not significant for the isotopes of a given element since they all have the same electronic properties.

The best relative precision for a single isotopic ratio determination on the LAMMA obtained to date is about 5% (one standard deviation). The isotopic ratios among the major isotopes of lead, which was present as a constituent of a thin glass film, were measured with the LAMMA. The relative standard deviations of the ratios for 10 separate spectra of closely spaced regions in the film ranged from 4% to 6% and were independent of whether the calculations of the ratios were based upon peak amplitudes or integrated peak areas.

The dynamic response of the transient waveform recorder that is used to digitize and store the mass spectrum is an important factor that affects the precision of isotope ratio measurements. Although the precision of the analog-to-digital converter may be 8 bits for input signals that vary slowly with time, the effective bit resolution is severely degraded when the measured waveform has major frequency components that approach the bandwidth of the recorder. Specific sources of error in analog-to-digital conversion that are frequency dependent include integral and differential nonlinearities, missing codes, and aperture uncertainty. Since the channel contents can change by a factor of 2 in adjacent channels when a mass peak is sampled at 10 ns per channel, it is clear that very high frequency components are present in the input signal train from the LAMMA. It has been found that the precision of the transient recorder for these pulses corresponds to 4 or 5 bits rather than 8. This completely accounts for the measured ratio precisions that are observed.

An example of the potential application of the LAMMA to isotopic analysis problems is the determination of the half-life of Re-187 by measuring the ingrowth with time of Os-187 in a sample of rhenium that has been spiked with a known amount of a reference isotope such as Os-190. For this experiment, the total quantity of Os-187 created in one year from 1 kg of rhenium is about 6 ng. With the current state-of-the-art, no other mass spectrometric technique can do a routine isotopic analysis of osmium with this amount of material.

As a test of the capability of the LAMMA to perform this type of measurement, an unknown set of samples of osmium chloride containing approximately 10 ng of osmium with non-natural isotopic composition was supplied by Dr. Manfred Lindner of Lawrence Livermore Laboratory. A similar sample of natural osmium was used to calibrate the nonlinear response of the electron multiplier detector. The correction factor for this effect was as large as 30% of the measured ratio for the conditions of this experiment.

A spectrum of the non-natural osmium sample is shown in figure 40. It is estimated that less than 1 pg of osmium was consumed in acquiring a single spectrum. Isotopic ratios were calculated from peak areas of 10 such spectra, corrected for detector nonlinearity, and averaged. The resulting values are shown in Table 39 along with the revealed isotopic composition of the sample. It is clear that the LAMMA is capable of determining isotopic ratios from less than 1 ng of osmium with an accuracy better than 3% when the ratio value is greater than 0.2. These preliminary results give confidence that the LAMMA can be used to improve the accuracy with which the half-life of Re-187 is presently known.

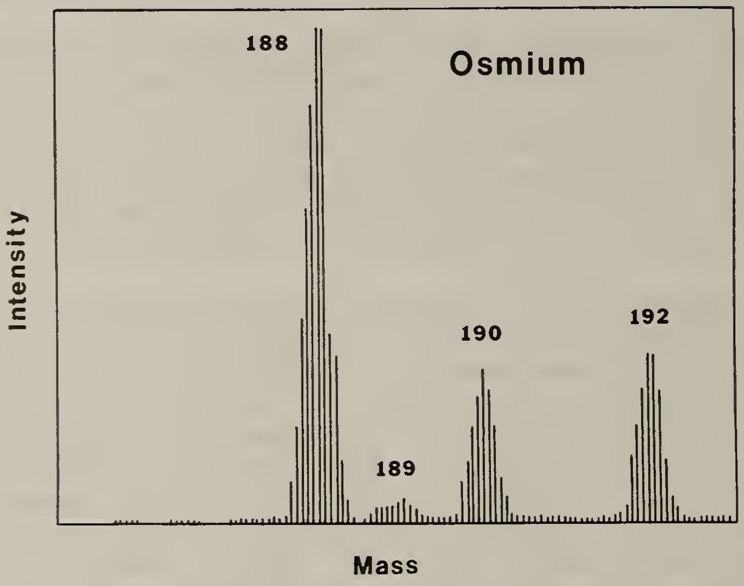

Figure 40. LAMMA spectrum of osmium with non-natural isotopic content.

Table 39. Isotopic Ratios of Osmium: Non-Natural Mixture.

Average of 10 Spectra

	189/188	190/188	192/188
Ratio determined by LAMMA	0.037 ±0.002[a]	0.233 ±0.008	0.263 ±0.007
Calculated ratio	0.031	0.232	0.256

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[a] One standard deviation of the mean.

2. Microbeam Analysis of Diffusion - Induced Grain Boundary Migration (51109)

D. E. Newbury

Diffusion-induced grain boundary migration is a recently recognized low-temperature phenomenon that can lead to unexpected grain boundary migration and vastly enhanced mass transport in polycrystalline materials. Diffusion of solute along grain boundaries can cause the boundaries to migrate and sweep across grains, mixing in solute at rates and concentrations which cannot be matched by ordinary lattice diffusion at the same temperature. In conjunction with members of the NBS Metullurgy Division (T. J. Piccone, D. B. Butrymowicz, J. R. Manning and J. W. Cahn), microbeam analysis techniques were used to study solute distributions at grain boundaries in polycrystalline copper annealed in the presence of zinc and arsenic vapors [1]. An x-ray area scan of a typical grain boundary area in the Cu-Zn system is shown in figure 41a, along with a line profile compositional trace, Figure 41b. The composition is found to vary with a wave-like periodicity with increasing amplitude toward the migrating boundary front. Note that the troughs of the waves coincide with the troughs actually visible in the x-ray area scan. In the studies with arsenic as a solute, it was further noticed that the sum of all elements detected dropped anomalously in the region of the migrating boundary, which suggested the presence of an undetected light element. This sample was examined by secondary ion mass spectrometry in the ion microscope with a cesium primary beam. Ion images for $^{16}O^-$ and $^{75}As^-$ indicated the coexistence of these elements in the region swept out by the migrating boundary, Figures 42a and 42b. By subtracting the sum of all elements found in quantitative x-ray microanalysis from 100%, the amount of oxygen incorporated in the copper was estimated to be of the order of 2-5 weight percent. This is a remarkable observation in view of the fact that the bulk solubility of oxygen in copper is only of the order of 0.01 weight percent. The oxygen may be present in the grain boundary region in the form of a finely divided copper oxide with a size below the spatial resolution of the analytical techniques. Further experiments on this and other systems are planned.

Reference

[1] T. J. Piccone, D. B. Butrymowicz, D. E. Newbury, J. R. Manning, and J. W. Cahn, "Diffusion-induced Grain Boundary Migration in the Cu-Zn System" Scripta Metallurgica, 16 (1982) 839-843.

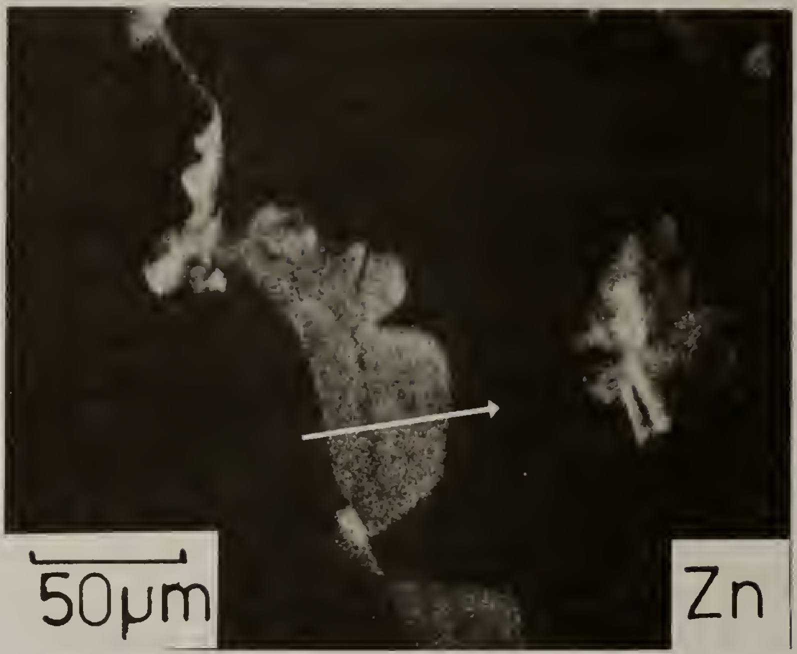

Figure 41a. X-ray area scan of zinc at migrated grain boundaries.

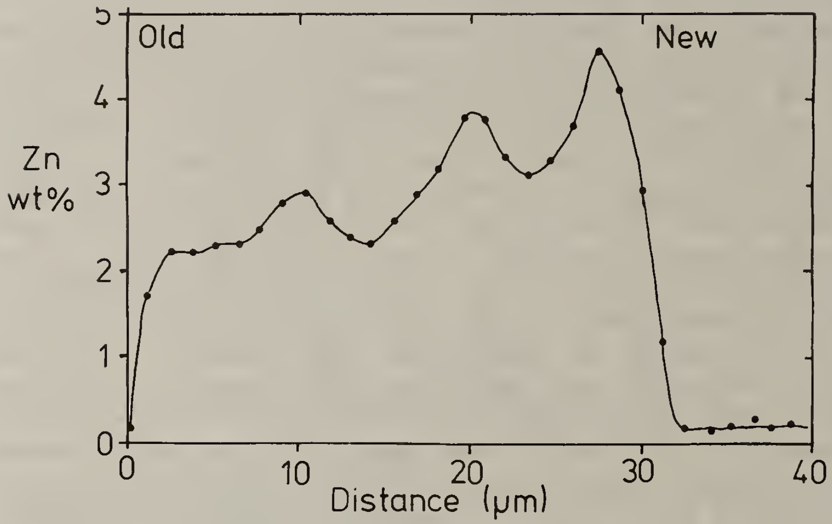

Figure 41b. Quantitative zinc line profile along Cu-Zn grain boundary.

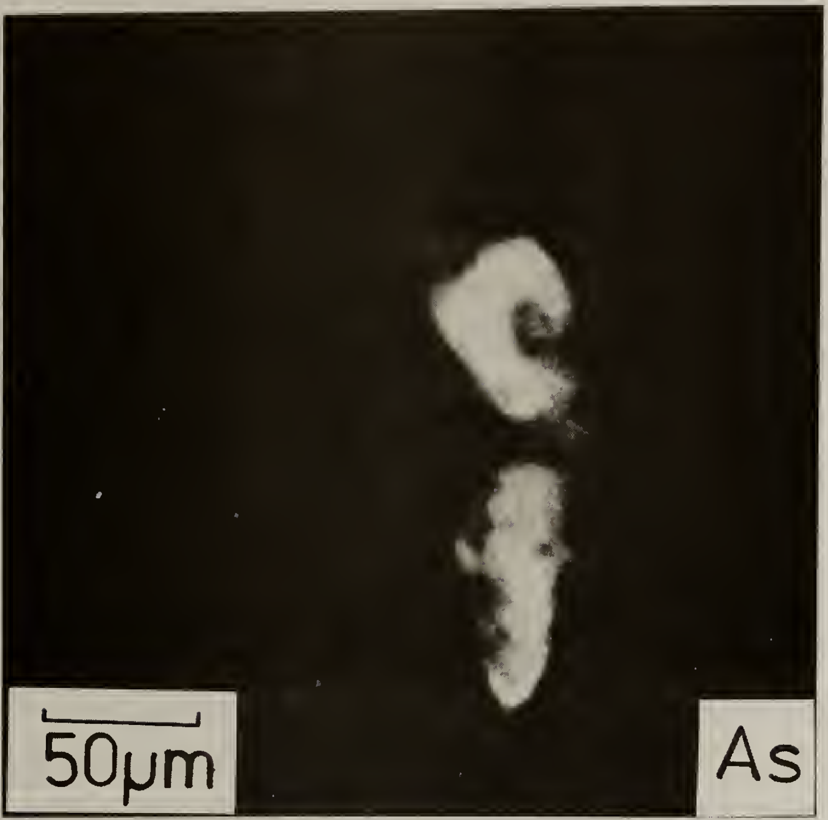

Figure 42a. $^{16}O^-$ ion microscope image of grain boundary.

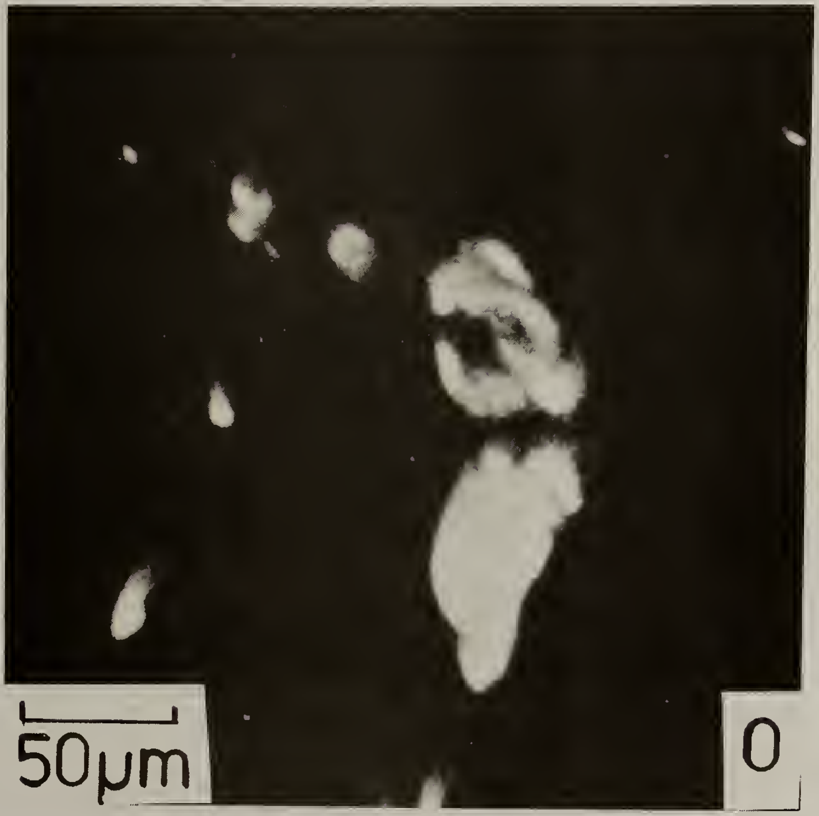

Figure 42b. $^{75}As^-$ ion microscope image of grain boundary.

3. Electron Beam Broadening in Thin Films of Uranium Alloys Analyzed in the Analytical Electron Microscope (11330)

R. L. Myklebust, D. E. Newbury

The spatial resolution of microanalysis by the technique of analytical electron microscopy is defined by a combination of the size of the primary electron beam and the degree of elastic scattering of the beam electrons. Various models have been developed for the calculation of beam broadening based on analytic descriptions of scattering (single, plural, and multiple regimes) and on discrete simulation of electron trajectories (Monte Carlo electron trajectory simulation). Previously, the available experimental data on beam broadening that are useful for testing these theories have been derived from specimens of low to intermediate atomic number (e.g., Al to Fe). Since the cross section for elastic scattering increases as the square of the atomic number, there is considerable interest in examining beam broadening in targets of high atomic number.

A series of experiments were carried out in conjunction with A. Romig of Sandia National Laboratory to measure beam broadening in alloys of uranium and to compare the results of those measurements with various model calculations. The U-Mo and U-Nb systems were chosen because in both of these systems, a lamellar eutectic is formed, providing sharp, planar interfaces between a pure uranium phase containing less than 0.1 wt% solute and a phase containing the alloying element (either U_2Mo intermetallic or U-12 wt% Nb solid solution). This sharp partitioning of the solute element provides an ideal marker for beam broadening. In the experiment, a beam of known diameter was stepped across a carefully oriented boundary. Energy dispersive x-ray spectrometry was used to measure the x-ray emissions at each location along a line parallel to the interface. A resulting profile is shown in figure 43. Monte Carlo calculations were performed with a simulation specifically adapted to the case of a planar interface. This simulation carefully considered the partitioning of scattering steps across the interface, and also considered the change in scattering power across the interface. The results of the calculation are also shown in figure 43. In general, the agreement realized between experiment and calculation is good. In the near boundary region, the profile is controlled mainly by the characteristics of the beam size, shape, and intensity distribution. The effects of scattering can be detected principally in the tail of the distribution. Additional experiments are planned to examine this portion of the distribution in greater detail. With this information, the analytic and Monte Carlo models for beam broadening can be refined.

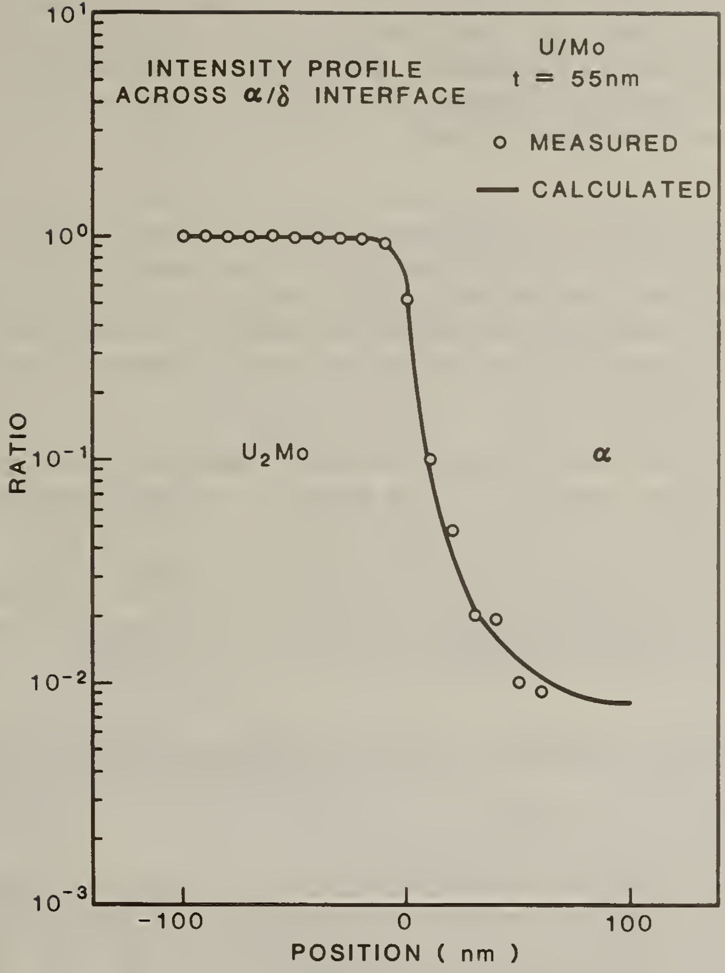

Figure 43. Molybdenum signal normalized to U_2Mo phase as a function of position across a U_2Mo/U interface.

4. Status of the Quantitative Electron Probe Microanalysis Programs FRAME and FRAME C (11330)

R. L. Myklebust, B. Thorne

The electron probe quantitative analysis programs, FRAME and FRAME C, have been under development in our laboratory for the past several years. FRAME computes the quantitative chemical compositional data for electron probe microanalyses obtained with crystal or wavelength dispersive spectrometers whereas, FRAME C computes the quantitative results for electron probe data obtained with an energy dispersive lithium-drifted silicon detector. These programs have been developed for specific instruments and in the computer language associated with that instrument. For example, FRAME C was written in FLEXTRAN to run on a Tracor Northern multichannel analyzer. Because of this, it has been difficult to transfer these programs from one computer to another without a great deal of effort.

During the past year we have reconstructed both programs to run on the VAX computer in Fortran 77. Since this is the new standard for Fortran, it was selected as the language for both programs. There may still be some minor differences among various computers, principally in the way files are read and written; however, these differences should not affect the use or results of the programs in any substantive way.

In the past, each version of FRAME C was written to operate on a specific, computer-based multichannel analyzer. This made each version unique. The new versions of both programs should operate on any computer that has Fortran. The user does have to give up the ability to process his data using functions on his multichannel analyzer and move the spectral data into a file on a computer. This is partially offset by greatly increasing the speed with which the data can be processed.

The programs have been tested and confirmed to operate properly. There is some documentation remaining to be added to the programs and some simple operating instructions left to write for the user, otherwise, both programs are complete. We have a rather large number of requests for the programs and we will begin filling these orders as soon as possible. Since both programs have been extensively described in the past, a publication consisting of only the source code together with some examples is planned.

5. Crystallographic Contrast in Ion Microprobe Analysis of Inconel (51109)

D. E. Newbury, D. S. Simons

Certain metallic alloy samples are known to exhibit crystallographic artifacts during Secondary Ion Mass Spectrometric (SIMS) analysis. That is, different crystal grains of a polycrystalline specimen show different absolute and relative ion yields of the major constituents, even though the elemental composition of each grain is identical. The effect has been seen most commonly in nickel-based alloys.

Several previous studies have illuminated various aspects of this problem. McHugh [1] demonstrated strong grain-to-grain variations in absolute ion yields of Fe, Cr, and Ni from an inconel sample under oxygen bombardment but claimed that relative sensitivities of these elements were essentially invariant. Bernheim and Slodzian [2] studied the angular dependence of secondary ion emission from a Ni-2%Cr single crystal under argon or oxygen bombardment, and with oxygen flooding of the surface. They found that Cr/Ni yields varied with angular position of the target and hypothesized that these variations were a consequence of differences in implanted oxygen concentration. Christie et al., [3] found that relative sensitivities of Fe, Cr, and Ni from nickel-based alloys vary with surface oxygen coverage and that these variations could be indexed by a matrix ion species ratio. Shiraiwa et al., [4] showed that crystallographic contrast exists in ion images of Fe, Cr, and Ni from high nickel-chromium steel and inconel under oxygen bombardment, but the contrast is eliminated when nitrogen is used as the sputtering ion.

We have incorporated the results of these previous reports into a comprehensive study of crystallographic contrast in the nickel-based alloy inconel

X-750. Individual crystal grains in a polycrystalline sample were characterized by electron channeling in a scanning electron microscope to determine their crystal orientations. Selected grains were then individually analyzed in an Applied Research Laboratory Ion Microprobe Mass Analyzer with oxygen bombardment to determine differences from grain to grain in sputtering rate, near-surface depth profiles, relative sensitivities of major species, and spectral indicators of oxygen concentration.

In figure 44, the closed circles represent the relative sensitivities, expressed as sensitivity factors, of iron and chromium with respect to nickel for 13 individual crystallites, measured at ambient instrument pressure. Each data point is plotted versus the measured ion ratio CrO/Cr_2 which was found to be a sensitive spectral indicator of oxygen concentration at the site of ion emission. The open circles represent data from the same crystallites taken at elevated oxygen pressure in the sample chamber. One notes that smooth curves (solid lines) can be drawn through the data with typical deviations of less than 10 percent (dashed lines).

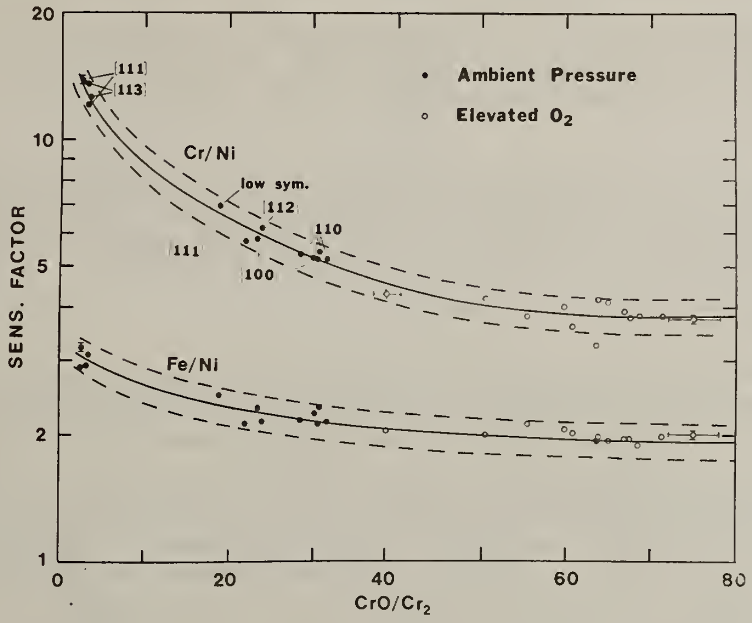

Figure 44. Relative sensitivities for Fe/Ni and Cr/Ni in various crystalletes of different orjentations plotted as a function of the measured CrO^+/Cr_2^+ secondary ion ratio.

Several observations can be drawn from this study. First, elevated oxygen pressure in the sample chamber nearly eliminates the grain-to-grain variations in the relative sensitivities of the major elemental constituents of inconel under ion bombardment. Second, the curves of figure 44 can be used to correct for crystallographic contrast under ambient instrument pressure by specifying relative sensitivity factors to be applied according to the measured ion ratio CrO/Cr_2 of an individual crystallite. Finally, figure 44, along with other data from this study, shows that crystallographic contrast in inconel arises from grain-to-grain differences in near-surface oxygen concentration.

The oxygen is incorporated by implantation from the primary oxygen ion beam and by surface deposition from gaseous oxygen in the sample chamber. Possible mechanisms for the influence of oxygen flooding on secondary ion yield include: (1) Compensation for sputtering rate differences due to orientation which leads to differences in the quantity of implanted oxygen at the sputtering front; and (2) Modification of ion channeling due to the formation of an amorphous oxide layer at the surface.

References

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6. Development of a Comprehensive Algorithm to Calculate the Spectral Output Distribution of X-Ray Tubes for X-Ray Spectrometry (11330)

L. Feng, P. A. Pella, J. Small

Several researchers have worked on fundamental parameter models for use in quantitative x-ray spectrometry. Perhaps the best known work in the field is that of Criss and co-workers of the Naval Research Laboratory, who developed a comprehensive computer program called NRLXRF to correct for x-ray absorption/enhancement effects in thick specimens. In such approaches, it is necessary to calculate the spectral output of the x-ray tube for excitation of the sample. Because parameters such as backscattering factors, fluorescence yields, and ionization cross sections are not known with sufficient accuracy, it is important to use measured x-ray output spectral distributions to develop a reliable algorithm. Most of the published x-ray tube spectra are somewhat restricted to a narrow range of tube voltages and target atomic numbers—NRLXRF, for example, uses approximations extrapolated from just a few x-ray tubes operated from 45-50 kV. We are currently working on an algorithm which generates the ratio of characteristic line x-ray intensity to continuum with the use of extensive experimental data measured by electron microprobe spectrometry. The data were obtained at various electron accelerating voltages from 10-40 kV and cover a wide range of atomic numbers. The detector used was a Si(Li) solid-state detector. From these data we have obtained preliminary fitting parameters for various targets as a function of atomic number and voltage to calculate the ratios of characteristic to continuum x-ray intensities. As an example, a comparison of the ratio of the K_α characteristic line intensity to continuum as a function of tube voltage for a chromium target tube are summarized in Table 40. The table includes values obtained from the NBS algorithm as well as experimentally determined values for spectral data at NBS, and values calculated from NRLXRF. The better agreement of the NBS calculated values with the experimental values as compared to NRLXRF at tube voltages less than 25 kV suggests that an improvement in the accuracy of the quantitative fundamental parameter approach may be possible.

Table 40. Comparison of Ratio of K_α Characteristic Line Intensities to Continuum as a Function of Tube Voltage for Cr Target Tube.

		Ratio	
kV	NRLXRF	NBS (Calc'd)	NBS (Expt'l)
10	1.595	2.373	2.300
15	3.436	4.071	4.350
20	4.792	5.279	5.250
25	5.903	6.201	6.050
30	6.845	6.938	6.700
35	7.661	7.549	--
40	8.390	8.871	7.550
45	9.041	8.53	--
			8.538[a]
			7.68[a]
			8.05[a]

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[a] Results from experimental work of other researchers at 45 kV.

7. Certification of Thin-glass Films as Standard Reference Materials for X-ray Spectrometry and Microanalysis (14210)

P. A. Pella, E. Steel

We have completed the mounting of over 200 glass films prepared by focused ion-beam sputtering in flat aluminum ring holders. Several films were selected for characterization from various runs in which the total mass loadings were about 172 µg/cm^2. These films (i.e., K-1612 glass) were each measured by energy-dispersive x-ray spectrometry to characterize the elemental homogeneity and composition for Al, Si, Ca, V, Mn, Co, and Cu. A film of about the same mass loading was selected for determination of microhomogeneity and for quantitation by electron probe microanalysis.

In Table 41 are summarized the x-ray intensities normalized to the total mass loading for the average of 13 films. The relative standard deviation of the set ranged from 1 to 1.5%. Electron probe data indicated that a trend in composition was noted from low to high for calcium and high to low for Si from the edge to the film center. The difference in composition from the high point to low point for calcium was 6% relative and 3% relative for silicon. The minor constituent elements, e.g., Co and Cu appeared to be evenly distributed. These results indicate that the overall uniformity as shown by electron probe microanalysis was satisfactory for certification of these films as NBS SRM's for x-ray spectrometer calibration. The final certification of these films will be accomplished after the compositions of a few selected films are analyzed by atomic absorption and neutron activation techniques.

Table 41. X-ray Intensity Normalized to Mass Loading for K-1612 Glass.

counts/μg/cm^2

Film #	Mass Loading μg/cm^2	Al	Si	Ca	V	Mn	Co	Cu
1-13								
Average	172.0	41.42	173.4	799	284	633	200	641
Std. Dev.	0.7	0.51	1.7	10	5.7	9.1	2.7	7
% RSD	0.4	1.2	1.0	1.3	1.5	1.4	1.3	1.1

We have finished the fabrication of another glass target (i.e., K-2084) containing Si, K, Ti, Fe, Zn, and Pb, and have prepared a few sets of sputtered films for evaluation. Several films were subjected to various conditions of humidity to test the film integrity. These films showed no evidence of deterioration even when subjected to hot water vapor. Therefore, this particular film composition was determined to be satisfactory for producing standard films. Electron probe microanalysis of the elemental microhomogeneity, however, showed serious problems in the uniformity from edge-to-edge for the elements Ti and Pb. Figure 45 shows a scan of the lead content of the film from edge-to-edge in 30-one mm step increments. There is about a 25 percent change in lead content over the film diameter. We are presently modifying the ion-beam instrument to allow some translation of the substrate stage in addition to rotation and in this way expect to achieve better uniformity of film composition.

Glass films are also being prepared for use as standards in microanalysis. These films are less than one micrometer thick and are mounted on 3 mm transmission electron microscope mounts. Previous work has shown that glass K-411 has sufficient homogeneity for a standard and this year the films' stability under high voltage electron beam bombardment in an analytical electron microscope was investigated. Under a fine point beam, the concentrations of Mg and Ca were low with respect to Si. However, under most other beam conditions, i.e., defocussed spot or rastered area, the film compositions are stable. Work is continuing by studying glasses of other compositions in order to determine the optimum sputtering conditions for preparing uniform thin films.

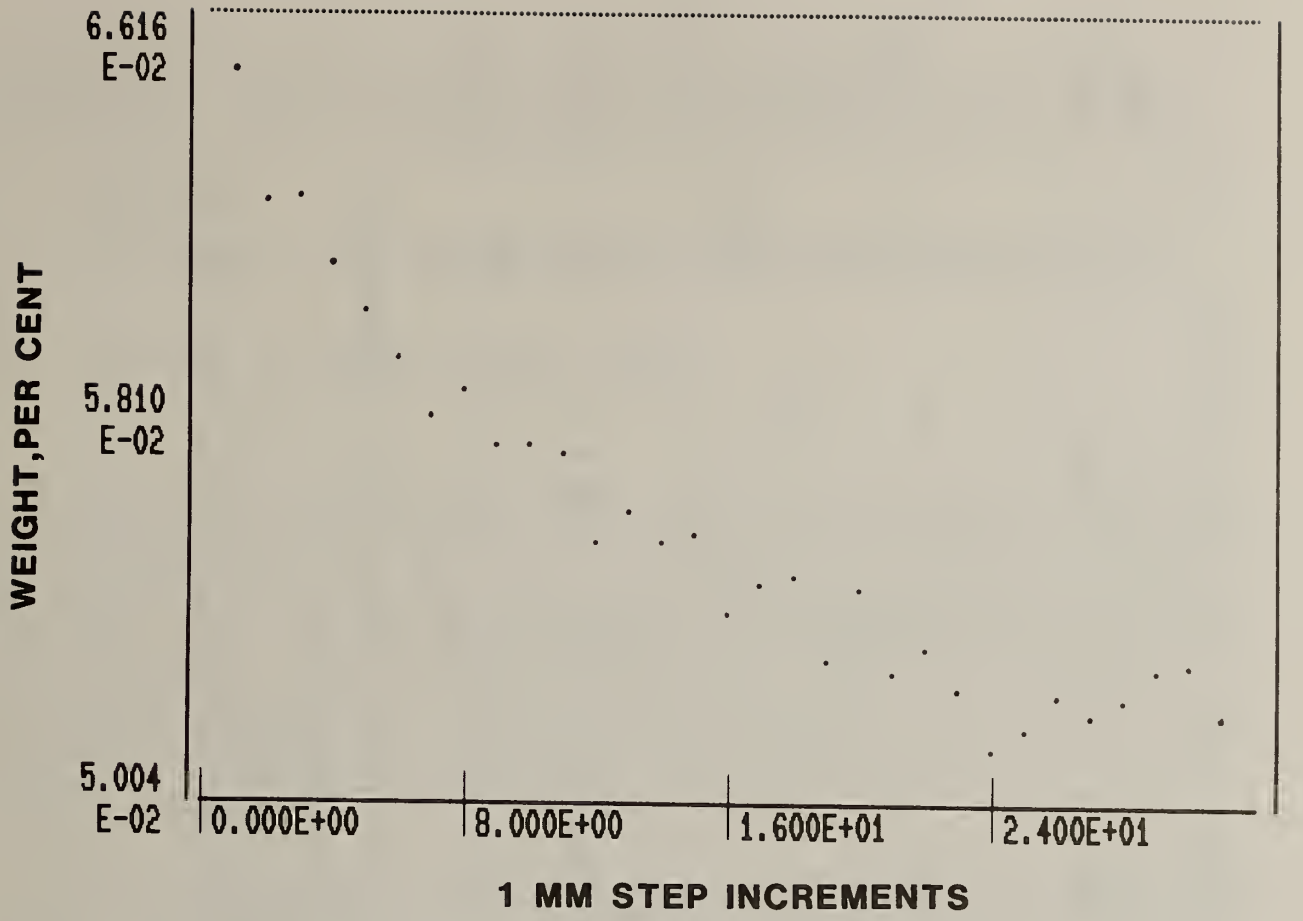

Figure 45. Lead content across film diameter.

8. X-Ray Spectrometric Analysis of NBS-SRM Bovine Liver and Pine Needles After Separation and Preconcentration (11330)

L. Feng, P. A. Pella, J. Sieber

A preconcentration method for the x-ray spectrometric analysis of trace elements in coal, urban particulate, and urine including detection limits has been described [1]. Chelex-100 was used to separate trace elements from alkali and alkaline earth; the separated metals were quantitatively loaded on cation exchange resin filters and subsequently determined by x-ray spectrometry. During the past year we have extended this method to the analysis of other types of biological samples such as NBS-SRM's 1577, 1577a, 1577b Bovine Liver and 1575 Pine Needles. We found that with little modification of our published procedure we could measure iron, manganese, copper, and zinc with an accuracy of ±10% as compared to the certified values. A summary of the results are included in Table 42. As shown in the table the recoveries for all elements except iron was better than 95%. Several sample dissolution techniques were investigated in an effort to improve the iron recovery. We found that temperatures of 300 °C or more were necessary in the perchloric acid digestion procedure to get better iron recovery. Analysis of NBS-SRM 1577 Bovine Liver using quartz and PFA Teflon for dissolution and digestion gave a

Table 42. Summary of Results for NBS-SRM's 1575, 1577, 1577a, and 1577b

	Mn, μg/g		Fe, μg/g		Cu, μg/g		Zn, μg/g	
Sample	Obs.	Cert.[a]	Obs.	Cert.[a]	Obs.	Cert.[a]	Obs.	Cert.[a]
Pine Needle								
1	656	675 ± 15	191	200 ± 10	2.8	3.0 ± 0.3	63	64.9 ± 5.5[b] (NAA)
2	659		190		3.1		63	
3	714		208		2.8		66	
4	648		196		3.1		69	
Average	669		196		3.0		65	
s[c]	30		8		0.17		2.9	
Bovine Liver								
1-1577a	10.5	9.9 ± 0.8	178	194 ± 20	159	158 ± 7	126	123 ± 8
2-1577b*	10.9		172		166		126	
3-1577	10.5	10.3 ± 1.0	148	268 ± 8	188	193 ± 10	134	130 ± 13
4-1577	10.5		152		190		137	

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[a] NBS certificates of analysis 1575, 1577, and 1577a, Pine Needles and Bovine Liver, respectively.

[b] Not a certified value, obtained by neutron activation analysis at NBS.

[c] Standard deviation of a single measurement based on n = 4 samples.

*NOTE: 1577b is intended as a renewal for 1577a and is believed to have the same composition for the above elements as 1577a.

result of 246 μg/g with an uncertainty of ±10 μg/g based on three replicate measurements. This represents a recovery of 92 percent. A technical paper describing this work is being prepared for publication in Analytical Chemistry.

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9. Evaluation of Personal Monitors (14210)

R. A. Fletcher

During the past two years, we have conducted research on the design and evaluation of a number of Personal Environmental Monitors (PEM's). As part of this project, laboratory evaluation of the NBS personal particulate monitor was completed last year. This year, field testing of the monitor has been undertaken, and the feasibility of incorporating simultaneous gas monitoring into the device is being studied. In response to a redefinition of inhalable particulate the monitor has been retrofitted with a new inlet and the unit has been recharacterized. The gas monitoring effort to date has involved evaluating a number of small NO_2 samplers. This report will discuss changes to the particulate monitor, describe field testing and detail the new gas sampling efforts.

The inhalable particle size range has been redefined from $\leq$15 μm to $\leq$10 μm aerodynamic diameter (A.D.), based on the Chan-Lippmann empirical inhalation curve. As a result, a 10 μm A.D. particle size cut (50% penetration) inlet modification was made to the NBS particle monitor. The cut characteristics were determined using laboratory generated monodisperse oleic acid particles containing a fluorescein dye tracer. Results indicate that the cut size is very close to 10 μm and well within the new inhalable criteria.

The NBS particulate monitor, with the 10 μm diameter inlet, was field tested at the University of Arizona (Tucson, AR). An EPA dichotomous particle sampler was employed as an EPA accepted reference monitor for ambient particulates.

Both monitors separate and collect fine ($\leq$3.5 μm) and coarse ($\leq$15 μm) size particles on filter substrates that allow gravimetric and chemical analysis. Gravimetric analysis was performed on both size fractions from the NBS and dichotomous samplers. These filters were subsequently analyzed for sulfate since ambient sulfate aerosol is predominately found in the fine particle size fraction and is therefore a good tracer for that size range. The agreement between the two monitors was good, with the total ambient particulate sulfate concentration agreeing exactly.

One of the most widely known passive NO_2 gas samplers is the Palmes tube. This diffusionally-limited sampler collects NO_2 on triethanolamine treated metal screens located at the closed end of a small tube. The NO_2 collection rate at quasi-static ($\leq$0.2 m/s) wind velocity was measured to be 96 percent of the predicted value.

The Palmes tube was tested at wind velocities of 1 and 2.4 m/s in the NBS wind tunnel test facility to determine its dynamic NO_2 collection efficiency. NO_2 was generated by oxidation of NO with air and was injected into the flowing stream of the wind tunnel through 9 jets equally spaced over a turbulent mixing grid.

A chemiluminescence detector was employed down-stream to measure the NO_2 concentration within the tunnel. The detector was calibrated daily with NBS permeation tubes.

The velocity and directional dependence is shown in figure 46. This figure shows the ratio of NO_2 collected by the Palmes tube to the amount that should have been collected based on the molecular diffusion rate of the gas in the tube and the NO_2 concentration in the air stream as determined by the chemiluminescence detector. Parallel wind orientation (X) did not affect the sampling rate, while perpendicular (O) orientation created a 10-15 percent increase in NO_2 collection efficiency. It is thought that turbulent mixing across the tube opening shortens the effective diffusion path and thus increases the NO_2 collection rate for the perpendicular case.

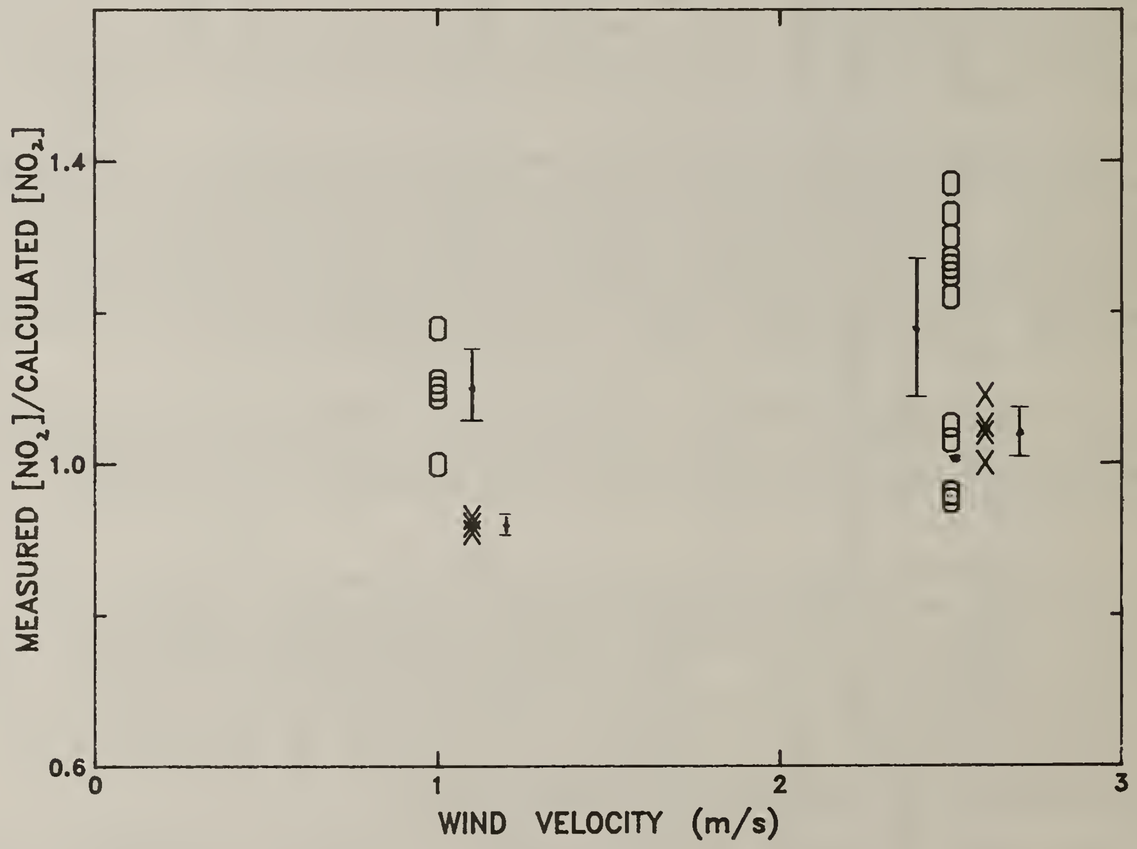

Figure 46. Palmes tube NO_2 collection efficiency as a function of wind speed. (O) denotes tube orientation perpendicular to the wind stream and (X) denotes orientation parallel with the stream. The bars indicate the relative standard deviation for each speed and tube orientation.

A number of passive gas samplers have been evaluated to identify a device with a high enough collection rate to be useful for low level environmental NO_2 monitoring. The sampler found to be most promising is a device in which the metal screen has been replaced with a glass fiber filter treated with triethanolamine. Evaluation test results are shown in figure 47 for a quasi-static wind velocity (≤ 0.2 m/s), NO_2 concentrations ranging from 0.08-3.1 ppm, and relative humidity values ranging from 15-70 percent. The collection rate was determined from the slope of a linear least squares fit to the data to be 5.3 μg NO_2/ppmh.

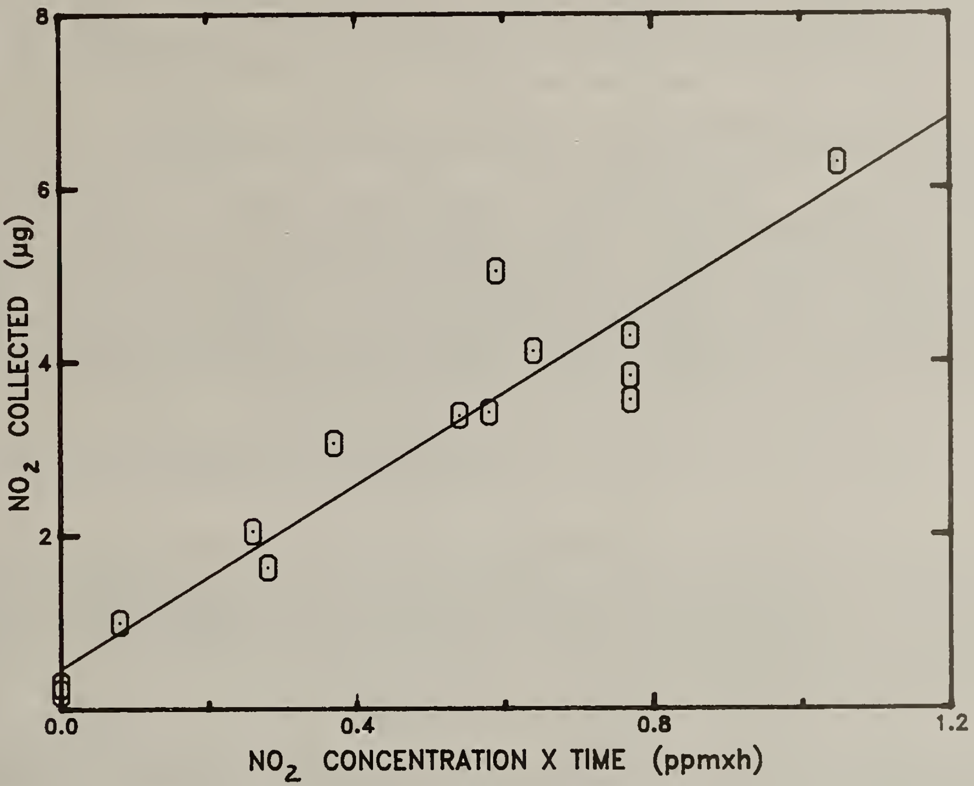

Figure 47. The rate of NO_2 collected as a function of gas concentration-exposure duration product. An unweighted linear least squares fit gives 5.3 μg/ppmh as the collection rate.

Small, passive gas samplers of this type can be used in conjunction with the NBS particle monitor to determine human exposure to noxious gases as well as inhalable particulates. This is an important advance in light of the numerous gas pollutants such as NO_2, CO, radon, formaldehyde, and organic vapors being found in homes and indoor environments where people spend the vast majority of their lives.

10. Measurement of the Temperature Dependence of the Ozone Absorption Cross-Sections in the Ultraviolet (11330)

A. M. Bass

The project for determination of the temperature dependence of the ozone ultraviolet absorption cross-sections is approximately two-thirds completed. As discussed in previous annual reports, a critical need exists in the upper-atmosphere research-community for accurate, detailed values of these cross-sections for analysis of observational data and for modelling calculations. We plan to determine these values over the wavelength range 200 nm to 700 nm and over the temperature range 200 K to 300 K. At the present time we have completed measurements over the wavelength region 250 to 340 nm (Hartley and Huggins Bands) at three temperatures: 295 K, 243 K, and 228 K. Measurements have been started at 273 K and will be completed during the coming year.

We have also completed detailed measurements of the temperature variation from 210 K to 295 K of the cross-sections at the wavelengths of the eight principal Dobson bands, used for ground-based observations of the ozone total column density. Dr. W. Komhyr (NOAA) and Dr. C. Mateer (Environment Canada) have applied these new data to the analysis of ozone data obtained from various sources and have concluded that the problem of inconsistent data obtained from different types of observations (Dobson, Satellite-BUV, SBUV) when using the older (1957 Vigroux) coefficients, appears now to be substantially solved by use of the new coefficients.

Extension of these measurements to shorter wavelengths, 200 to 250 nm, is important for application to observations at high altitudes in the mesosphere. Those measurements will be done in the coming year, as well as extension of the temperature range to the lowest value we can achieve in the present apparatus (about 210 K).

11. Completion of Reference Ultraviolet Photometer for Ozone Calibrations (11330)

A. M. Bass

For several years NBS has maintained a 3-meter long ultraviolet photometer to be used as a national standard for calibration of ozone monitors. The photometer, which operates on the principle of the absorption of ultraviolet mercury radiation (253.7 nm) by ozone, has been operating satisfactorily and has been providing calibration services for federal and state agencies and for private industry. The accuracy of the 3-meter photometer is estimated to be about ±2%, the uncertainty coming mainly from the uncertainty in the value of the ozone absorption cross-section at 253.7 nm. The imprecision of the concentration determination is estimated to be about 10% relative at 50 ppb, and decreasing to about 0.5% relative at the highest concentration used.

In 1979 the U.S. Environmental Protection Agency promulgated a new calibration procedure for ozone based on ultraviolet absorption photometry. The EPA recently requested our assistance in the design and construction of a new photometer to serve as a primary standard for the EPA laboratories. This work, which was done in collaboration with Dr. R. Paur of EPA, is nearly finished. A photometer of novel design has been constructed, and testing and calibration are underway now in our laboratory.

The new standard is a double-beam photometer with an effective path length of about 172 cm. Absorption of the 253.7 nm line of the mercury spectrum by ozone is determined by means of a very sensitive detection system. From the measured absorbance and known path lengths, application of the Beer-Lambert law yields the value of the ozone concentration in the sample. The temperature and pressure of the sample of ozone in air are continuously recorded and corrections for these parameters are automatically made. The entire measurement process is controlled by a desk top computer, and the data are automatically reduced and stored on magnetic tape.

Preliminary testing of the new instrument in the EPA laboratories in North Carolina and at NBS has confirmed that the performance of the photometer is in accordance with or better than design specifications. Over the range of concentrations from 100 to 1000 ppb of ozone in air the precision of the concentration determination is better than ±0.3%. The accuracy of the measurement is limited to approximately ±2% principally because of the cross-section uncertainty mentioned above. A detailed intercomparison of the 3-meter long photometer and the new standard instrument is now underway in our laboratories.

12. Photoacoustic Detection of HCl (11330)

Alan Fried

Hydrochloric acid (HCl) is believed to be a key atmospheric species present both as a hygroscopic gas and as a liquid acid aerosol. This molecule plays a pivotal role in the movement of chlorine across the air-sea interface and into the gas phase in the troposphere. In the stratosphere, HCl acts as a critical, photochemically inert reservoir for chlorine atoms cycling through a complex series of O_3 destruction reactions. Unfortunately, our basic understanding of the role that HCl plays in the atmosphere is founded on very few measurements. Because of the rather low ambient background concentrations and the reactive hygroscopic nature of the HCl molecule, meaningful atmospheric measurements require a detection system meeting several stringent criteria: (1) detection of HCl in the ppb range, (2) high selectivity from many potential interfering species, and (3) detection in a manner that preserves the integrity of the HCl concentration in the probed volume (i.e., no sample perturbation due to losses and/or chemical interactions on instrument surfaces).

The goal of our research was to develop a sensitive photothermal detection system for continuous real-time measurements of HCl in the lower troposphere. The results reported here represent the initial phase of this research with a prototype laboratory system. In this study, a discretely tunable deuterium-fluoride (DF) laser was used to selectively excite HCl transitions in the 3.6 - 4.1 μ atmospheric spectral window. The strongest absorption, occurs at 3.63 μm between the P(6) absorption line of $H^{37}Cl$ and the $P_2(3)$ laser transition.

The output of the DF laser, operating at a 1 pulse-per-second repetition rate, was focused into the center of a glass photoacoustic cell, schematically shown in figure 48. Sound waves, associated with the rapid conversion of the laser absorbed energy into translational modes, were detected with an electret microphone sealed in the cell wall. Amplified signals from the microphone were subsequently fed into an oscilloscope for visual display or processed by a boxcar integrator, and read out using a strip chart recorder.

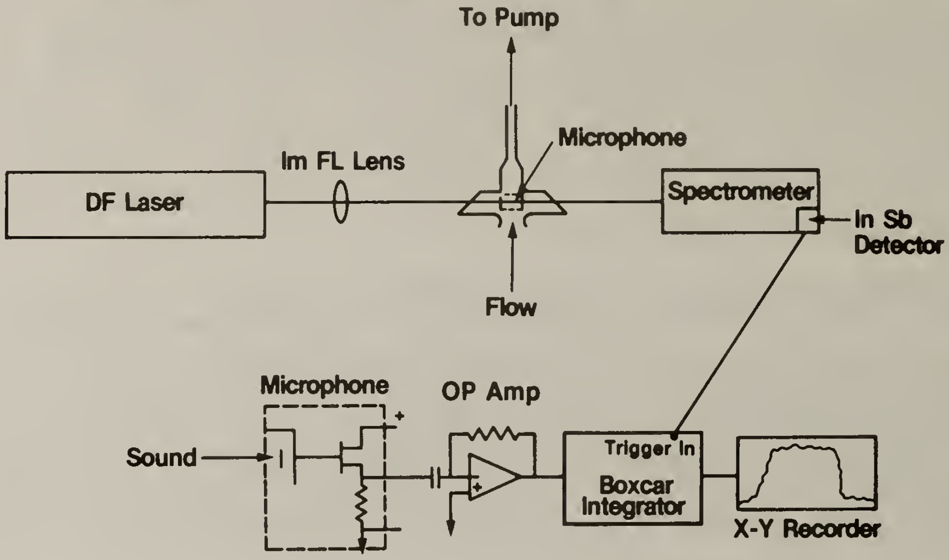

Figure 48. Schematic of photoacoustic HCl analyzer.

Trace concentrations of HCl in air were continously drawn through the photoacoustic cell. The flow was directed perpendicular to the axis of the laser beam, as shown in figure 48. Trace mixtures were generated by diluting cylinder HCl, at a nominal cylinder concentration of 50 ppm in N_2, with air in a glass mixing chamber close to the photoacoustic cell inlet. The concentration of HCl at the cell inlet was determined by bubbling the gas through solution and performing acid-base titrations. An independant acid-chloride determination was made by diverting the flow through ultra-pure nylon filters. The quantitatively trapped acid-chloride was subsequently measured by neutron activation using the 1642.0 and 2167.0 keV ^{38}Cl gamma-ray peaks.

Although these two techniques were very useful in the present study in providing us with independent HCl calibrations, they are not specific enough for HCl to be used directly in the ambient atmosphere.

In accordance with theory, the measured photoacoustic response shows a linear relationship with HCl concentration. From a linear-least-squares fit of these data and independent noise measurements, we deduce that the minimum detectable HCl concentration falls within the range 66-108 ppb. The sensitivity, however, was enhanced by approximately a factor of 2, yielding a predicted detection limit in the range of 50 ppb when ambient air at 44 percent relative humidity was used as the diluent gas in place of dry cylinder air (H_2O=157 ppm). In this more realistic mode of operation, the signal amplitude increased because of the unique nature of water vapor in collisionally quenching vibrationally excited HCl. In contrast, using dry cylinder air, the relaxation of HCl and hence the generation of sound, occurs on a much longer time scale; this results in a dramatically lower signal amplitude. At the HCl concentrations used in these comparisions direct absorption of the laser by H_2O and HDO were found to produce negligible interference, and thus can be ruled out as the cause of this signal enhancement.

Although our present detection limit is substantially above our goal, we are investigating several enhancement techniques that should lower this detection limit well below 1 ppb. At this sensitivity, we will not only have the capability to assess anticipated spectral interferences, heretofore not observed, but also will be able to demonstrate novel techniques to minimize their effect.

13. A Study of Measurement Interference In The Photoacoustic Detection of NO_2 By Argon-Ion Laser Excitation (11330)

Alan Fried

Nitrogen dioxide (NO_2) is a molecule of major importance in the chemistry of the atmosphere. As with all molecules of atmospheric interest, there has been an on going quest for development of increasingly more sensitive and selective detection methods for studies in both the ambient environment and the laboratory. Over the past few years, we have been actively involved in developing and employing sensitive photoacoustic detection techniques for measuring NO_2 in various laboratory studies (figure 49). In one such study [1], we employed photoacoustic detection for measuring NO_2 concentrations produced in the gas phase titration (GPT) of nitric oxide (NO) with ozone (O_3) in accordance with the bimolecular reaction:

$$NO\ (\text{excess}) + O_3 = NO_2 + O_2 \tag{1}$$

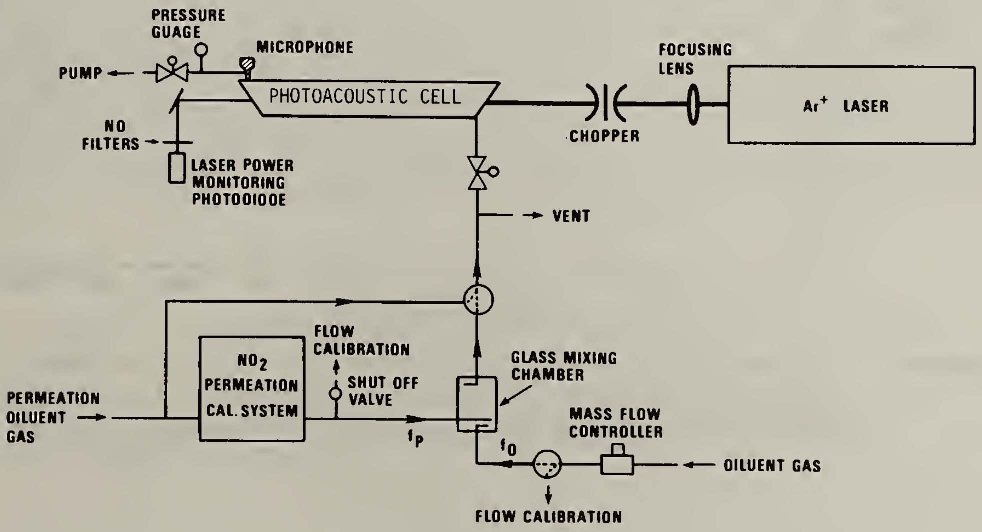

Figure 49. Photoacoustic detection system for NO_2.

The 488.0-nm line from an argon-ion laser was used as the excitation source. Since NO is transparent at this wavelength, NO_2 can be measured directly without an interfering response from NO. Despite this discrimination, photoacoustic detection of NO_2 at 488.0 nm, and for that matter throughout the entire visible region suffers from a lack of information regarding potential interferences. The present investigation was designed to study interferences by the major species present in the GPT experiments: NO, O_3, O_2, N_2 and H_2O vapor. In this study, two types of interferences were considered: (1) interference by direct absorption of the 488.0 nm laser line and (2) interference by energy transfer to metastable states of the matrix gas with a concomitant loss in photoacoustic response.

Interference by direct absorption of the laser was studied by flowing each of the gases of interest directly into the photoacoustic cell, bypassing the permeation calibration system. Base line signals measured in this manner for pure N_2, pure O_2, a 50 ppm NO/N_2 mixture and for H_2O vapor concentrations ranging from 20 ppm up to an estimated concentration of 0.3% were all found to be identical. Interference by energy transfer was studied by directing the matrix gas of interest over the permeation tube into the photoacoustic cell and recording the resulting NO_2 response. The NO_2 photoacoustic responses in pure N_2 and in the 50 ppm NO/N_2 mixture were found to be identical. The response in pure O_2, however, was markedly lower. The decreased response caused by O_2 was found to be independent of NO_2 concentration but clearly dependent on the O_2 concentration, as shown in figure 50.

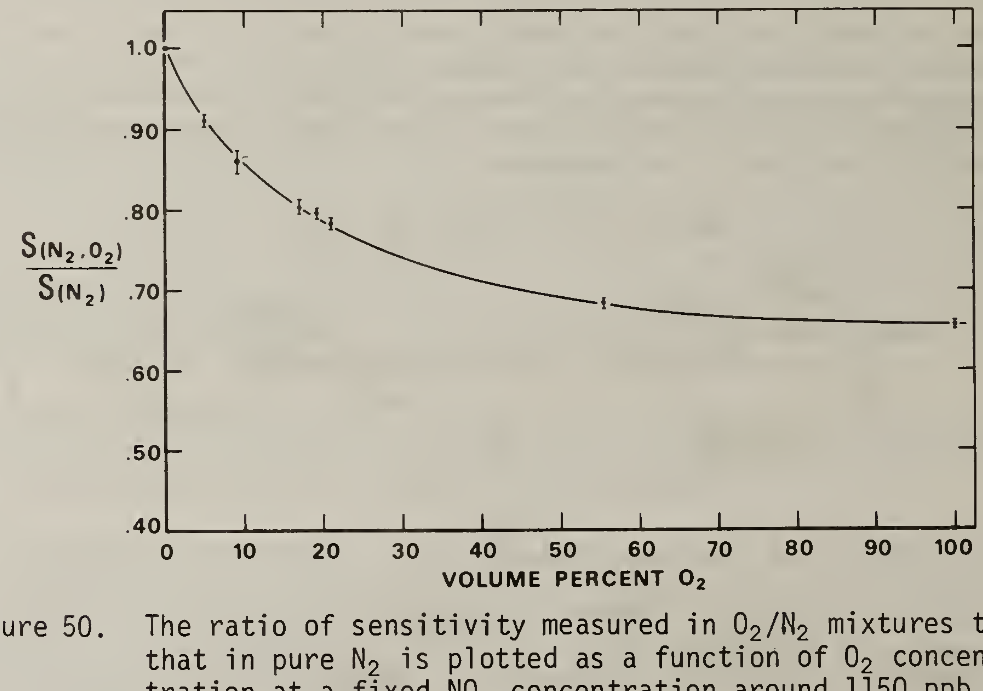

Figure 50. The ratio of sensitivity measured in O_2/N_2 mixtures to that in pure N_2 is plotted as a function of O_2 concentration at a fixed NO_2 concentration around 1150 ppb.

As can be seen, the decrease in response is dependent on the O_2 composition, having a pronounced slope at low O_2 concentrations and reaching a limiting value at high concentrations. This O_2 effect can be reduced by adding H_2O vapor in the 100-200 ppm concentration range. Higher concentrations of water vapor around 0.3%, resulted in complete signal recovery. These results are only preliminary and more studies are neededto quantify the effect.

Such behavior, however, is related to the fact that H_2O vapor, is an effective quenching partner. In the case of quenching electronically excited NO_2 (NO_2*), H_2O vapor has been found to be ∿6 times more effective than either O_2 or N_2 [2].

One interpretation of these observations is that H_2O vapor effectively competes with processes which in the presence of O_2 short-circuit the mechanism responsible for generation of heat, namely $NO_2^*+M \nrightarrow NO_2+M$. One such process consistent with the observations above, is that of energy transfer. In such a mechanism, energy is transferred from NO_2^* to the metastable $O_2(^1\Delta_g)$ electronic state of O_2 in accordance with:

$$NO_2^* + O_2(^3\Sigma_g) \rightarrow NO_2 + O_2(^1\Delta_g). \qquad (2)$$

The $^1\Delta_g$ state of O_2 is extremely long-lived, having a radiative lifetime of about 45 minutes, and based on a quenching rate constant of 2.2×10^{-18} $cm^3 \cdot mol.^{-1} \cdot sec^{-1}$ at the O_2 pressures used in this study (600 torr), the collisional relaxation lifetime is on the order of 23 ms. Since the chopping period used in the present study was much shorter than this (1/250 Hz) the energy thus transferred to $O_2(^1\Delta_g)$ would be effectively trapped, thereby reducing the total amount of energy degrading to heat during the "on" period of each chopper cycle and hence reducing the photoacoustic response.

The results presented in this preliminary investigation significantly impact on photoacoustic measurements of NO_2 carried out at 488.0 nm and perhaps at other visible wavelengths. The determination of NO_2 concentration from such measurements, both in the laboratory and in the atmosphere, would be in error unless precautions are taken to insure that the matrix gases are of similar composition in the measurement and calibration phases, as was the case in the gas phase titration measurements carried out concurrent with this study. Small differences in O_2 content, however, as might be expected from different air cylinders, would cause a negligibly small effect.

References

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14. Accelerator Mass Spectrometry (AMS) (11330)

L. A. Currie, G. A. Klouda

Since the First Conference on Radiocarbon Dating with Accelerators (Rochester, 1978), research and applications of AMS have burgeoned. Dedicated tandem accelerators have been ordered or installed in at least five different countries; and applications to atmospheric science, archeology, hydrology, tectonics, glaciology, geology, oceanography, and cosmochemistry are underway with a host of long-lived nuclides ranging from ^{10}Be to ^{129}I. The technique has revolutionized the measurement of natural and artificial long-lived radionuclides through the direct measurement of isotope ratios (to $\sim 10^{-15}$) rather than specific radioactivity.

For ^{14}C, AMS provides an increased sensitivity of about 10^5 compared to conventional radiocarbon dating techniques. Thus far, the NBS program in Environmental Radiocarbon represents the only application of AMS to atmospheric carbonaceous aerosols, and our experiments at Rochester and Tucson are unique also in terms of sample size (<100 μg-carbon) and carbon isotope separation-implantation as a linked ("hyphenated") technique. Our first experiment at Rochester was designed as an exploratory evaluation of sample preparation techniques and the application of a conventional tandem van de Graff to the measurement of small samples (<500 μg-carbon) containing natural levels of radiocarbon. Our just-completed experiment at the University of Arizona represented the first use of that "dedicated" tandem to unknown samples, and it demonstrated the capability of that machine to measure submilligram samples to an accuracy of $\sim$10%. (The subsequent installation of an improved sample holder at Tucson has improved this figure to 3-5%).

A summary of our Tucson data is given in Table 43, in which accelerator parameters and radiocarbon results are tabulated for a series of standards, blanks and carbonaceous aerosol samples. The importance of these results is two-fold: (1) samples as small as 100 μg (contemporary radiocarbon) can be measured with an accuracy of $\sim$10%; (2) individual chemical fractions of carbonaceous aerosols with as little as 100 μg can be assayed by AMS-thus complementing our miniature gas counter measurements (>5 mg-carbon) at NBS. This hundredfold increase in sensitivity means that isotopic carbon measurements may be used for high resolution (time, space, composition, particle size) studies of multiple sources of carbonaceous gases and aerosols as opposed to our prior work which focussed on the gross discrimination of fossil from biogenic carbon sources.

Table 43. Results of Accelerator Mass Spectrometry-Environmental Radiocarbon Measurements. (Tucson, May 1982)

Sample	Approximate Mass (μg-carbon)	Observed Percent Modern-C (± s.d.)	Percent Contemporary (Living) Carbon (± s.d.)	Relative Error (%)
Dating - SRM's (Oxalic Acid)				
RM 49	1000	1.22 ± 0.06	---	-11
RM 49	100	1.20 ± 0.16	---	-12
SRM 4990B	1000	1.15 ± 0.09	---	+10
Urban Dust SRM (SRM - 1649)				
Elemental Fraction	50	0.32 ± 0.08	0.25 ± 0.06	---
Remote Aerosol Sample[a] (Colorado)	500	0.87 ± 0.05	0.69 ± 0.04	---
Los Angeles Aerosol[a]	∿50	0.48 ± 0.17	0.37 ± 0.13	---

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[a] Collaborative NSF project with the Colorado School of Mines.

15. Receptor Modeling and Radiocarbon in Aerosols: Source Apportionment (11330)

L. A. Currie, R. W. Gerlach, G. A. Klouda

Important progress in both experimental and theoretical studies of carbonaceous aerosol sources has taken place during the past year. Cooperative work with a number of laboratories, in this country and abroad, has made possible the collection of samples representing a variety of sites and circumstances, and a pattern of fossil/biogenic carbon contributions is consequently emerging. The theoretical exercise took place specifically at the request of the EPA and it was designed to evaluate the strengths and limitations of current methods of source apportionment based on multispecies analysis of receptor (aerosol) samples.

Experimental investigations of ^{14}C in air particulate samples, carried out with the NBS mini gas proportional counting system, are summarized in Table 44 for three classes of sampling regions. The percentages of contemporary carbon listed correspond to the median values for a range of individual samples. Examination of these data show that, with certain important exceptions, the urban aerosols were largely fossil in origin, whereas the rural samples were mostly biogenic. Special exceptions are Portland, Utah-oil shale lands, and Barrow. In these three studies, radiocarbon measurements have given definitive confirmation to other data (emissions, meteorology, chemical composition) that the aerosol carbon has unusual contributions from: wood-burning (Portland), oil shale dust (Utah), and transpolar European aerosols (Barrow).

Table 44. Radiocarbon Dating of Atmospheric Particles.

Sampling	Location	Contemporary-C (%)	Comment
(Sub)urban	Salt Lake City	28	
	Denver	29	"Brown Cloud"
	Houston	34	
	Los Angeles	39	
	Portland, OR	77	Vegetative Burning
Rural	Utah — Oil Shale Lands	64	Baseline Data
	— Desert	88	
	Abastumani (USSR)	80	
	Shenandoah Valley	92	
Remote	Barrow, AK	27	"Arctic Haze"

Considerably more information concerning source types and strengths has been gained from temporal and compositional patterns for the various regional samples. In figure 51, for example, the time sequence is shown for the EPA (1980) study in Houston. Some common trends are clear from this exhibit, as well as an apparent coordinated discontinuity in slope. That is the increase (on Sept. 13) of total carbon and Pb together with the decrease in ^{14}C and

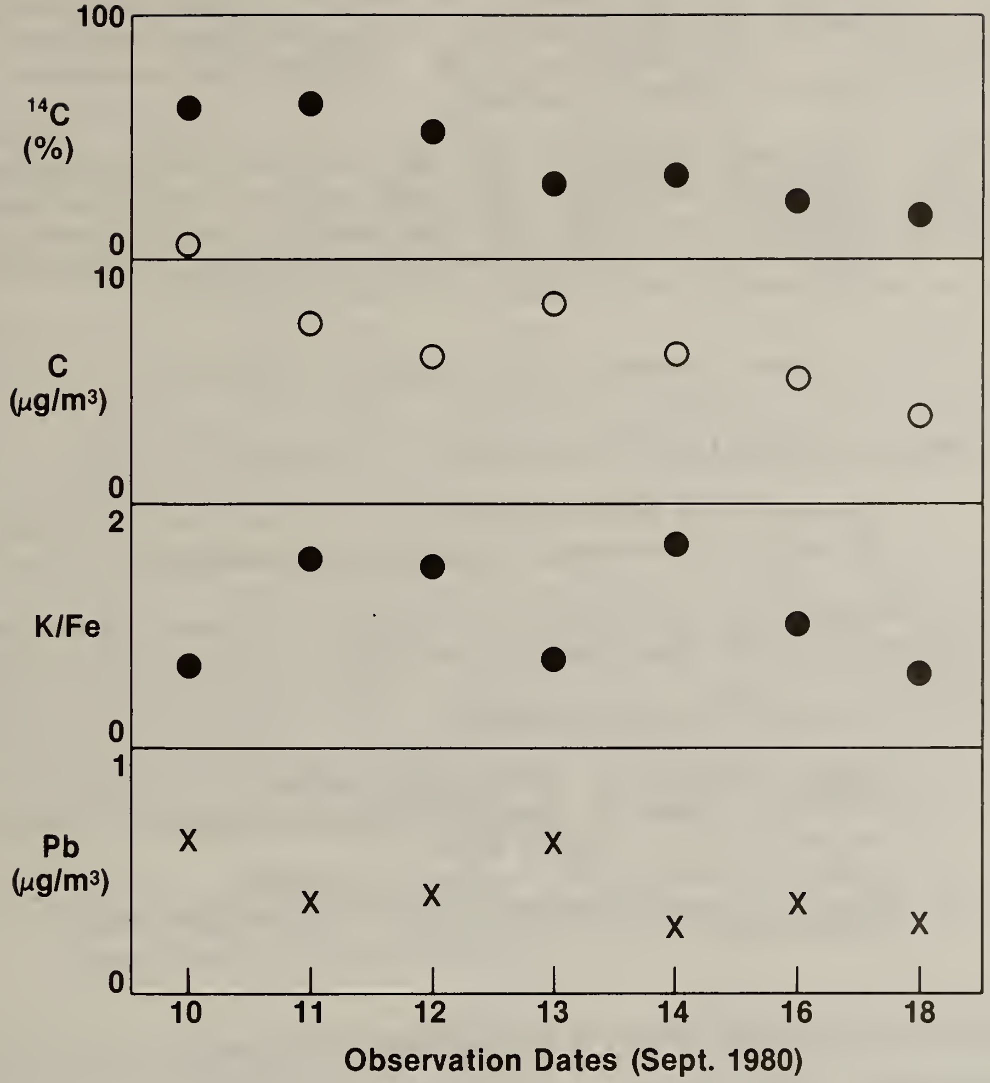

Figure 51. Houston — receptor data.

K/Fe suggests an injection of automotive (as opposed to vegetative) carbon on that day. The generally high ^{14}C values as well as K/Fe ratios has caused some re-thinking about possible vegetative carbon sources in the Houston area, one likely candidate being the burning of rice hulls.

Quantitative source apportionment of samples such as those collected in Houston is accomplished by receptor modeling (RM) techniques. A detailed laboratory intercomparison of the accuracy and precision of RM took place this spring through the use of a simulation data set generated in our laboratory. This exercise was based on realistic source profiles, and dispersion behavior, real meteorological data, and known source strengths and error structure. Using this simulated data set we were able to evaluate different models (ridge regression, factor analysis, weighted least squares, . . .) employed by some nine laboratories, and draw conclusions regarding the strengths and weaknesses of the alternative models. Highlights from our analysis of both the simulation process, itself, and from the laboratory performances are given in

Table 45. It appears that this sort of data intercomparison exercise bears an importance for complex analytical chemical data evaluation procedures ("Chemometrics") which is a direct analogue to SRM intercomparison exercises for the evaluation of analytical chemical methods.

Already it has demonstrated the need for far more careful treatment of uncertainties in receptor modeling, and it has shown how improved design of the measurement process--including individual particle analysis and isotopic analysis, for example--can minimize source mis-assignments and break the collinearity which greatly limits sensitivity and precision.

Table 45. Conclusions: Simulation Process.

- Data proved suitable for realistic, reliable tests of:
    - Deconvolution method resolving power, accuracy, limitations
    - RM design requirements (sampling, measurements)
- Dispersion model inadequate for emission data use; plume size, variability too great; no line sources
- Future exercises should include:
    - Direct replication, sensitivity studies
    - Multiple receptors, geographic (source,receptor) information
    - Morphological, isotopic data
    - Extended "world list", number of unknowns
    - Discrete feedstock changes, modified sampling schedule (0700/1900)

16. Methodology for Vapor Pressure Measurements of Organics in the 10 to 10^{-5} Pascal Range (14210)

E. Hughes, G. Sleater, W. Zielinski

Research was carried out to evaluate methodology proposed by the U.S. Environmental Protection Agency (Federal Register 45-227, pp. 77345-77350, 21 November, 1980) for use by the chemical industry for the determination of the vapor pressure of organic compounds in the 10 to 10^{-5} Pascal range. The proposed methodology was developed by Stanford Research Institute under EPA contract in an attempt to standardize methodology for vapor pressure data on new chemicals which, under law (Toxic Substances Control Act), industry must provide to EPA prior to industrial production of new chemicals.

The proposed methodology, based on gas saturation by the test chemical, the time-integrated adsorption of the gas on a suitable solid sorbent, its quantitative desorption and analysis by a suitable analytical technique, was thoroughly examined experimentally by NBS. The study revealed that the greatest uncertainty of the proposed method involves the desorption step prior to analysis. Desorption efficiency was found to vary as a function of sorbent characteristics, the accuracy and methodology of loading test compounds on the sorbent for desorption efficiency determinations, the nature of the extraction solvent used for desorption of that compound, the loading level of the test compound on the sorbent, and the desorption time. To illustrate, using maleic anhydride as the test compound and charcoal as the sorbent, gas chromatographic (GC) peak area (arbitrary units) varied for six different desorption solvents from about 2,900 (CS_2) to 35,400 (acetone) after a 1-hour desorption time, with no GC peak obtained after a 17-hour desorption time. Desorption efficiency for naphthalene from charcoal varied with naphthalene loadings (NL) from about 35% (0.8 mg NL) to about 45% (2.5 mg NL).

Further research investigated variables associated with the experimental gas-saturation system and the measurements. These included proper alignment of the heating lamps in the constant temperature chamber for improved temperature control, flow-rate calibration and measurement correction as a function of ambient temperature and pressure, and other factors contributing to measurement system stability and method standardization.

The detailed research findings were provided to participants (8 laboratories) involved in an NBS-coordinated round-robin to assess inter- and intralaboratory variance for the proposed EPA vapor pressure method. Research was also carried out to evaluate an alternate method for vapor pressure measurements. The alternate method, which does not use a sorbent, is based upon direct capture of the vapor of the test compound in a cold solvent trap which was then directly subjected to analysis. An intercomparison of the two methods is given in Table 46. A final assessment of the proposed method will be made at the conclusion of the round-robin study.

Table 46 Intercomparison of Proposed EPA Method and Cold Trap Method for Vapor Pressure Determinations.

Test Compound	Number of Replicates	Test Temperature °C	Vapor Pressure (Pascals)[a] Cold Trap	Proposed Method
Naphthalene	15	30.0	17.8 (2.1)	
	8	30.0		18.0 (2.7)
Naphthalene	2	35.2	26.8 (1.2)	
	4	35.2		36.8 (0.9)
Maleic Anhydride	9	30.0	56.1 (10.2)	
	6	30.0		57.4 (14.4)
Benzophenone	9	30.0	0.120 (0.08)	

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[a] Average value (standard deviation).

17. Development of Multicomponent Toxic Organics-in-Air Standards (14210)

W. Cuthrell, W. P. Schmidt

Stable standards are required to maintain and verify the quality assurance of low concentration toxic organic vapor measurements needed to assess personal exposures in the industrial workplace atmosphere. Research efforts on the development of single component standards have now led to the completion of the certification of concentration and stability for benzene gas cylinder Standard Reference Materials (SRM's) at 9.76 and 0.25 parts-per-million (ppm) by mole, respectively.

Preliminary work on the preparation of ppm multicomponent toxic organic mixtures using a recently developed microgravimetric approach revealed that a variable number of components of the mixture gave significant deviation (±2% relative) between their calculated and analyzed concentrations. This procedure was based upon initial preparation of small glass tubes containing weighed amounts (0.1-10 mg) of specific organics (one organic/tube), heat-sealing the tubes, introducing 4-6 tubes in a teflon sleeve connected to an evacuated gas cylinder, and breaking the tubes inside the sleeve to load the cylinder with the weighed organics. The cylinder was then pressurized with the matrix gas (nitrogen) and subsequently analyzed by gas chromatography against reference standards. Because of the observed deviations, this procedure was modified to include the cooling of weighed sample tubes with dry ice prior to sealing and loading the evacuated cylinder one tube at a time using a 1/8-inch Teflon sleeve. The modified procedure gave no significant deviations between calculated and analyzed concentrations for any organic studied so far. Originally, only five or six organic compounds could be added to a cylinder. Based on the success of the improved procedure, as many as 20 compounds can now be added to a single cylinder if the need should arise.

The preparation of ppb level gravimetric mixtures has been accomplished through the use of smaller organic compound sample weights (0.1 mg) or, in some cases, the use of larger cylinders (150 rather than 30 cubic feet) to allow using larger sample weights (greater precision) and still obtain the same dilution. Binary and tertiary organic cylinder mixtures have been compared with more concentrated organic cylinder mixtures, and the concentrations have been found by analysis to agree well with those predicted from the gravimetric data (e.g., Table 47).

Furthermore, individual gas mixtures prepared to contain vinyl chloride, chloroform, benzene, toluene, tetrachloroethylene, and chlorobenzene have shown no evidence of changes in concentration over the past two years. These individual mixtures will serve as the basis for future toxic organic vapor SRM's.

More recently, a set of gravimetric organic gas mixtures containing four aromatics (benzene, toluene, chlorobenzene, and bromobenzene) at the 10 ppb to 2 ppm (by mole) concentration levels has been prepared to assess the feasibility of issuing such a mixture as an SRM. No problems were encountered in preparing and analyzing this set of mixtures. Determination of their stability is now in progress.

Table 47. Comparison of Gravimetrically-Calculated and Analyzed Standards for Low (<200 ppb) Concentration and High-Capacity Cylinder Mixtures.

Cylinder Capacity (ft^3)	Organic Levels, ppb					
	Vinyl Chloride		Benzene		Tetrachloroethylene	
	Calculated	Analyzed	Calculated	Analyzed	Calculated	Analyzed
30	73	72	—	—	—	—
30	—	—	45	47	—	—
30	—	—	—	—	141	142
150	227	222	258	251	—	—
150	—	—	24	22	9712	9700
150	638	633	840	834	1038	1040

As an adjunct to the development of trace organic constituent standards in cylinders, research was carried out on the feasibility of developing such standards in permeation tubes. Investigation of long-term storage parameters indicated that the only problem was the external absorption of the permeated organic by the polymer (Teflon) of the permeation device when stored in a static (non-flow) system. When permeation tubes were stored in this manner, it was noted that, during subsequent use in a constant air flow system, the device required up to seven weeks to return to its certified permeation rate. It is hence being recommended that users of such organic gas standards store permeation tubes in a slowly, continuously-flowing system.

Future work in this program will focus on the generation of multicomponent toxic organic standard mixtures in cylinders at the sub-ppm level, and the preparation of sub-ppm level standards for more volatile organics (e.g., chloroform, carbon tetrachloride).

18. Standards for Measurement of Atmospheric Carbon Dioxide - (11330)

E. Hughes, R. Myers, G. Sleater

Work on Standard Reference Materials (SRM's) for analysis of atmospheric carbon dioxide has progressed in two areas: the evaluation of the accuracy of the standards and the analysis of the SRM's. The question of accuracy has been addressed through preparation of a new series of gravimetric standards and by comparison of NBS-analyzed samples to the analysis of the same samples analyzed at Scripps Institute of Oceanography (SIO) last year. The samples which will ultimately become SRM's have been obtained and analyses are in progress.

A number of gravimetric standards have been prepared which duplicate those previously prepared, and which extend the range above and below the existing standards. These new standards have been intercompared with the older standards, and the agreement between the calculated concentration and the measured concentration, is as good as would be predicted from the agreement among the earlier gravimetric standards.

These gravimetric mixtures constitute a precise and presumably accurate set of standards. The precision can be evaluated from the analytical data, but the accuracy can only be estimated from the known sources of error. Since the possibility always exists that some source of error might go unnoticed, it is essential that some independent confirmation of the concentration be available. We had reported in last years report on such an independent confirmation, involving three samples which were analyzed using the manometric technique. These early results suggested a possible bias between values determined by the two measurement systems (NBS and SIO) of about 0.1 ppm. Consequently, six more samples were analyzed by SIO during March of 1982 and the results confirmed an apparent relative bias of about +0.16 ppm. The results of the second analysis are shown in Table 48.

Table 48. Comparison of Analysis by NBS and SIO Concentration of Carbon Dioxide in ppm.

Sample No.	NBS[a]	SIO[b]	Δ NBS-SIO
1	335.80	335.62	+ 0.18
2	335.56	335.47	+ 0.09
3	342.54	342.36	+ 0.18
4	342.88	342.64	+ 0.24
5	351.30	351.14	+ 0.16
6	351.32	351.03	+ 0.29
		Average	+ 0.19

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[a] Analyzed by comparison to gravimetric standards.

[b] Analyzed by absolute manometric measurement of each component.

The differences shown are consistent with those previously observed. It should be noted at this point that the NBS values were calculated assuming that the reagents used to prepare the gravimetric samples were 100% pure. This was known not to be an exact assumption; thus considerable effort has been expended in analyzing the purity of the reagent air and carbon dioxide. The carbon dioxide was determined to be 99.91% pure, with the principal impurities being nitrogen, oxygen, and water vapor. The analyses were performed using mass spectrometry and gas chromatography. The problem of determining the purity of the air was not so straight-forward. Gross impurities, other than carbon dioxide, affect the calculated concentration of carbon dioxide only in so far as they affect the assumed molecular weight of air.

Such gross impurities can be easily recognized, and in this case none were found present. The presence, however, of minute quantities of carbon dioxide affects the calculated value directly.

The reagent air had been stripped of the carbon dioxide by passage through "Ascarite" with the assumption of complete carbon dioxide removal. Attempts to prove the validity of the assumption were difficult. Replicate measurement by several techniques, including gas chromatography, non-dispersive infrared measurements, and catalytic reduction of the carbon dioxide followed by gas chromatographic measurement of the methane generated yielded a variety of results varying from zero to 2 ppm CO_2 in the air. After much effort, consistent values of 0.16 ppm were obtained by two of the methods. Taking into account the purity of the carbon dioxide (99.91%) and the concentration of the CO_2 in the reagent air, the total correction to the NBS values (C NBS) would be (C NBS-0.16). If all assumptions are correct, the NBS and SIO results are now indistinguishable from each other.

19. Development of Protocols for Providing Traceability of Commercial Gas Standards to NBS SRM Gas Mixtures (14210)

E. Hughes, G. Rhoderick

The purpose of the Certified Reference Material (CRM) program is to increase the availability of accurate gas standards. The CRM's, being secondary standards, are related to appropriate SRM's and the CRM concentration must be within ±1% of the SRM concentration. The CRM's are to supplement the existing SRM stock and are intended for traceability for gas mixtures at concentrations of a complementary SRM.

The manufacturer produces a batch of CRM's related to SRM's of a given concentration. The batch is analyzed by measuring one member as an internal standard against the SRM and then analyzing the other CRM's in the batch against the batch standard. An auditor, in this case Research Triangle Institute (RTI), selects two samples which are analyzed against the appropriate SRM. All data is sent to NBS for review and statistical analysis. NBS determines whether all requirements are met according to previously established criteria [1].

During the past year, nine batches of carbon monoxide in nitrogen consisting of 205 CRM's, two batches of carbon monoxide in air consisting of 53 CRM's, and one batch of nitric oxide in nitrogen consisting of 17 CRM's have met the requirements for Certified Reference Materials. Table 49 gives the contents, nominal concentrations, manufacturer, number of CRM's and date for each batch.

In addition to those listed in Table 49, there are three batches of nitric oxide in nitrogen and three batches of carbon monoxide in nitrogen which are still undergoing analysis and investigation.

Table 49. Certified Reference Materials

CRM Content	Manufacturer	Nominal Concentration	Number of Samples	Date Completed
CO/N_2	Matheson	50 ppm	11	2/5/82
CO in Air	AIRCO	42 ppm	17	2/9/82
CO/N_2	AIRCO	1000 ppm	11	3/2/82
CO/N_2	Scott	1000 ppm	36	3/3/82
CO/N_2	Scott	250 ppm	30	3/15/82
CO in Air	Scott	42 ppm	36	3/15/82
CO/N_2	AIRCO	2400 ppm	17	3/16/82
CO/N_2	AIRCO	8%	11	4/26/82
CO/N_2	Scott	10 ppm	36	4/28/82
NO/N_2	AIRCO	500 ppm	17	5/21/82
CO/N_2	Scott	25 ppm	36	5/21/82
CO/N_2	AIRCO	5000 ppm	17	7/22/82

The main problem of the program is indicated by the data of the nitric oxide-in-nitrogen CRM's. The 100 and 1000 ppm nitric oxide-in-nitrogen CRM's appear to be unstable. Additional measurements are being made to try to determine whether the disagreements are due to imprecision or instability. Table 50 shows data for the 1000-ppm batch as analyzed by the manufacturer. The data shows that several samples have decreased in concentration from one analysis to the next. This behavior suggests that some samples are unstable, but it would be difficult to prove that the lot is either stable or unstable.

Samples whose concentrations had decreased at each succeeding analysis appear to be unstable. If this decrease of about 0.5% in six months is real, then after one year's time, the concentration would decrease by 1%, which would not be tolerable for a CRM. Accordingly, the batch should be analyzed again three months from the last analysis. The 100 ppm nitric oxide-in-nitrogen batch reflects the same type of behavior and it too is to be reanalyzed.

Another problem which has been observed is due to the imprecision of measurement by the producer. A batch may be measured several times but the imprecision of measurement makes it difficult to recognize stability or variability problems.

Table 50. Data for 1000 ppm NO/N_2 of CRM vs. Internal Standard.

Sample No.	Concentration[a] 12/17/81	Concentration[a] 1/25/82	Concentration[a] 6/7/82	Differences[a] 6/7 - 12/17
1	954.1	953.3	951.6	-2.5
2	954.1	955.4	953.6	-0.5
3	953.8	954.0	953.5	-0.3
4	953.3	953.8	956.7	+3.4
5	955.0	954.7	950.8	-4.2
6	953.8	953.6	950.0	-3.8
7	953.7	953.1	952.4	-1.3
8	953.0	954.0	955.7	+2.7
9	954.4	953.5	952.2	-2.2
10	955.4	954.9	954.2	-1.2
11	953.9	955.4	954.7	+0.8
12	955.0	955.4	055.5	+0.5
13	955.6	954.6	954.7	-0.9
14	954.2	955.7	955.6	+1.4
15	954.5	955.4	954.7	+0.2
16	954.6	955.6	956.7	+2.1
17	954.3	953.5	951.5	-2.8
18	953.3	954.5	953.8	+0.5

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[a] Concentration is in parts per million by mole.

Most of the certifications have gone very smoothly with no problems. The manufacturer and RTI have agreed very well on almost all of the CRM batches, see Table 51. The uncertainty for the concentration of a batch has been between 1.0 to 1.2% on the average, with only a few having a somewhat higher uncertainty.

Appendices for the Procedure on CRM's have been written for carbon monoxide, nitric oxide, and sulfur dioxide, the last two having been completed this past year. The Appendix for propane has been written and submitted for approval.

Reference

[1] Hughes, E. E. and J. Mandel. A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards' SRM's. NBSIR 81-2227, NBS EPA-60017-81-010, May 1981.

Table 51. Comparison of Manufacturers' and Auditors' Concentrations

CRM	Manufacturer	Concentration, ppm by mole		Percent Difference
		Manufacturer	RTI	
50 ppm CO/N_2	Matheson	47.2 ± 0.6 ppm	47.3 ± 0.5 ppm	0.2
50 ppm CO/Air	AIRCO	42.4 ± 0.5 ppm	42.4 ± 0.5 ppm	0.0
1000 ppm CO/N_2	AIRCO	946 ± 9 ppm	944 ± 9 ppm	0.2
1000 ppm CO/N_2	Scott	970 ± 7 ppm	972 ± 7 ppm	0.2
250 ppm CO/N_2	Scott	240.0 ± 2.4 ppm	244.4 ± 2.4 ppm	0.1
42 ppm CO/Air	Scott	42.7 ± 0.4 ppm	42.7 ± 0.4 ppm	0.0
2400 ppm CO/N_2	AIRCO	2400 ± 24 ppm	2414 ± 24 ppm	0.4
8% CO/N_2	AIRCO	7.70 ± 0.08%	7.72 ± 0.08%	0.3
10 ppm CO/N_2	Scott	9.90 ± 0.11 ppm	9.94 ± 0.11 ppm	0.4
25 ppm CO/N_2	Scott	24.3 ± 0.3 ppm	24.3 ± 0.3 ppm	0.0
500 ppm NO/N_2	AIRCO	470 ± 5 ppm	470 ± 5 ppm	0.0
5000 ppm CO/N_2	AIRCO	4682 ± 47 ppm	4691 ± 47 ppm	0.2

20. Design and Evaluation of a High-Rate Passive Sampler for Ambient Levels of Nitrogen Dioxide (11330)

B. Cadoff

Passive gas samplers are used to measure time-average concentrations of pollutant gases and vapors. These devices sample the atmosphere through mass transport of the gas by diffusion or permeation with subsequent trapping on an appropriate absorbing chemical or surface. Generally, these samplers have been devised for the industrial environment where concentrations of particular gases may be one to two orders of magnitude higher than in non-industrial ambient atmospheres. We have developed a high-rate sampler, employing triethanolamine as the absorbing agent, that can obtain adequate samples of NO_2 in a few hours or less at ambient concentrations.

The sampler is constructed from a Nuclepore 47 mm aerosol holder which is fitted with a Nuclepore 0.8 μm polycarbonate membrane. A fiberglass disc containing triethanolamine is placed beneath the membrane. The base of the aerosol holder is capped with a polyethylene stopper. Before sampling, the sampler is kept in an air-tight enclosure (such as a jar). To sample ambient air, the sampler is removed from the jar. The total exposure time is recorded, and the sampler is placed back in its container for subsequent laboratory analysis.

The analytical work-up is done directly inside the sampler; the method utilizes Saltzman reagent to produce a violet-colored solution. This procedure has been adapted from one reported by Palmes et al., [1].

Table 52 shows representative data obtained over a range of concentrations of NO_2, at two levels of relative humidity, and varying ratios of NO/NO_2. It is seen that the concentration of NO has no effect on the sampling of NO_2 and that there is no effect on changing the relative humidity level from 20 percent to 60 percent. The sampler gives consistent results for concentrations of NO_2 ranging from 61 to 329 ppb, and sampling times as short as 1 hour. It can be seen (Table 52) that the ratio of NO_2 measured to the integrated exposure (A/B) varies only slightly, indicating a good consistency of sampler performance for all conditions.

Table 52. Laboratory Evaluation of High-Rate Personal Sampler for Nitrogen Dioxide.

NO_2 (ppm)	Exposure (hr)	NO/NO_2	Percent R. H.	Integrated Exposure (ppm-hr) [B]	NO_2 Found (μg) [A]	Ratio A/B
0.061	1.00	5.5	20	0.061	0.815	13.4
0.078	1.00	7.6	60	0.078	1.06	13.6
0.329	1.00	6.3	20	0.329	4.29	13.0
0.260	2.47	12.1	60	0.641	8.26	12.9
0.124	4.60	5.0	60	0.578	7.28	12.6
0.129	4.60	4.8	20	0.595	7.32	12.3
0.074	12.00	7.6	20	0.888	10.3	11.6

The lowest integrated exposure investigated was 0.061 ppm-hr. However, it is estimated that integrated exposures of approximately one-fifth this amount can be measured; or stated another way, an exposure to 12 ppb for one hour should be measurable with this sampler. A paper describing these results is currently in review for submission to Analytical Chemistry [2].

References

[1] Palmes, E. D., Gunnison, A. F., DiMattio, J., and Tomczyk, C. Am. Ind. Hyg. Assoc. J., 1976, (37), 570.

[2] Cadoff, B. C. and Hodgeson, J. "Design and Evaluation of a High-Rate Passive Sampler for Ambient Levels of Nitrogen Dioxide", to be submitted.

21. Development of Mixtures of ^{36}Ar and ^{40}Ar for Characterization of the Atmosphere of Venus (11330)

W. Dorko, G. Rhoderick

Several mass spectrometers and gas chromatographs were involved in the U.S. Pioneer and Russian Venera missions to Venus in 1978. The interpretation and correlation of the data produced by these instruments was difficult to perform to the required degree of accuracy. To resolve this difficulty, several standards for intercalibration of the instruments were needed. Due to the importance of these experiments, NASA asked NBS to prepare two mixtures (Table 53) consisting of Argon-36 and Argon-40 in a matrix of carbon dioxide. The critical factors were that the ^{36}Ar to ^{40}Ar ratio be known with an uncertainty of less than 0.5 percent relative, and that the ratio be close to unity.

Table 53. $^{36}Ar/^{40}Ar$ Mixtures Requested.

Concentration, ppm by mole

Component	Mixture 1	Mixture 2
^{36}Ar	25 ± 2	50 ± 4
^{40}Ar	25 ± 2	50 ± 4
CO_2	balance	balance

The best method of producing the mixtures would be by gravimetrically blending pure gases into cylinders. However, due to the weighing limitations of the analytical balances and the low concentration level of the argon in the final mixtures, they could not be blended directly. Hence, an intermediate mixture was made, from which the final mixtures were produced. The basic procedure used to prepare mixtures 1 and 2 was as follows:

(a) each of the three reagent gases was procured by NBS and analyzed to determine the type and the amount of the impurities.

(b) weighed amounts of ^{36}Ar, ^{40}Ar, and CO_2 were added to two evacuated cylinders to produce mixtures "A" and "B" which were numerically 5000 ppm ^{36}Ar and 5000 ppm ^{40}Ar in CO_2.

(c) weighed amounts of mixture "B" were added to two other evacuated cylinders, after which weighed portions of CO_2 were added to produce mixtures 1 and 2.

Because it was not practical to monitor the weight loss/gain of cylinders during the blending process, the mixtures were compounded by observing partial pressures to get to nominal concentrations, while the final results were calculated from the weight data. A special blending manifold was developed for preparing the "A" and "B" mixtures. There was a possibility that some of the argon isotopes were not quantitatively flushed into the sample cylinder.

Therefore, after the final addition of the CO_2, gas potentially trapped at two locations in the manifold was analyzed for argon to adjust the calculations.

To calculate the concentrations in cylinders "A" and "B", it was necessary to know the weights of the ^{36}Ar, ^{40}Ar, and CO_2 added, and the impurities in these individual gases (note: an impurity of ^{36}Ar was found in the ^{40}Ar). After correcting for impurities, the concentrations of ^{36}Ar and ^{40}Ar in "A" were determined to be 0.5051 (±0.0006) and 0.5078 (±0.0004) respectively; those for "B" were determined to be 0.4922 (±0.0006) and 0.4946 (±0.0004), respectively. The $^{36}Ar/^{40}Ar$ ratio determined by gas mass spectrometry agreed well with that determined from the mixing data, thereby confirming the blending results.

The final two mixtures were prepared and the concentrations were determined (Table 54) after correcting the ^{40}Ar concentration for the amount of that impurity found in the matrix carbon dioxide. Gas mass spectrometry was also used to confirm the argon isotope ratios of the final mixtures. The values obtained for these mixtures were well within the requisite specifications. Mixture 1 was then transferred into four cylinders and mixture 2 transferred to four other cylinders resulting in four sets of two cylinders each. The four sets were forwarded to NASA; NASA then forwarded two sets to Russia.

Table 54. $^{36}Ar/^{40}Ar$ Standard Mixtures Prepared.

	Concentration (ppm by mole)		Ratio
Mixture	^{36}Ar	^{40}Ar	$^{36}Ar/^{40}Ar$
1	24.70 ± 0.04	24.93 ± 0.03	0.9908 (±0.0015)
2	49.12 ± 0.07	49.46 ± 0.05	0.9931 (±0.0015)

22. Development of Parts-per-Billion Nitrous Oxide-in-Air Standard Reference Materials (14306)

J. W. Elkins, E. E. Hughes, P. A. Johnson, R. L. Sams (550)

Three major areas of concern motivated our interest in undertaking the development of gas mixtures containing nitrous oxide (N_2O) in air at ambient concentration levels (270-330 ppb) as Standard Reference Materials (SRM's): (1) the effect of N_2O on reducing stratospheric ozone; (2) the "greenhouse" effect of N_2O on climatic changes; and (3) the role of N_2O in the Earth's nitrogen cycle. Recent figures released by the National Research Council [1] indicate that a doubling in the atmospheric concentration of N_2O may result in about a 10% reduction in stratospheric ozone (twice the reduction predicted for a doubling of freons F-11 and F-12), which would decrease the screening effect of stratospheric ozone for harmful solar ultraviolet radiation reaching the Earth's surface. Further, N_2O has strong infrared absorption bands in the "atmospheric window" which results in a stronger "greenhouse" warming effect per mole for N_2O increases than for atmospheric carbon dioxide increases (current models predict a global temperature rise of 0.7 K for N_2O doubling

(∿300 up to 600 ppb) and a 2.9 K for CO_2 doubling (∿300 to 600 ppm [2]). In addition, biologists are interested in ascertaining the transformation rate of ammonium to nitrate in studies of the Earth's nitrogen cycle by measuring changes in N_2O concentration [3].

The research strategy in the development of these SRM's has been initially to prepare gravimetric standards at ppm-levels, then dilute to ppb-levels by gravimetry. Verification of assigned concentration values is being based on intercomparing standards using electron capture-gas chromatography (EC-GC) and tunable diode laser-infrared spectroscopy (TDL-IR). Table 55 shows a comparison of results for concentration in various standards by both EC-GC and TDL-IR. The calculated concentrations (Meas. Conc.) shown refer to the predicted values from a plot of detector signal versus gravimetric concentration. A set of 15 gravimetric standards at ppb-levels were prepared from four different ppm-level gravimetric standards. Intercomparison of the standards against each other by EC-GC showed that the reproducibility of the preparation of gravimetric standards was better than ±0.15% (maximum range). An initial set of SRM's has been analyzed, with reproducibility of replicate samples of better than ±0.2% (maximum range). Therefore, it appears that individual SRM's of N_2O-in-air should be certifiable to ±0.5% (two standard deviations). Homogeneity studies of our initial set of SRM's of the same nominal concentration, indicate that each cylinder must be certified separately.

Infrared techniques offer the possibility of not only comparative measurements (e.g., Table 55), but also for absolute determinations of concentration. We are currently in the process of determining individual intensities for lines in the ν_3 band system of N_2O. This infrared parameter (along with total pressure, temperature, and pathlength measurements) will give independent verification of concentration values.

Table 55. Comparison of Electron Capture-Gas Chromatography (EC-GC) and Tunable Diode Laser-Infrared Spectroscopy (TDL-IR) Measurements N_2O Gravimetric Standards (GRAV).

		- - - GC-EC - - -		- - - TDL-IR - - -	
Sample #	Grav. Conc. (ppb)	Meas. Conc. (ppb)	Δ %	Meas. Conc. (ppb)	Δ %
1	259.7	259.7	0	259.7	0
2	275.1	275.1	0	274.8	-0.1%
3	284.2	284.0	+0.07%	284.4	-0.07%
4	323.7	323.2	-0.15%	323.7	0

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Currie, L. A., "Synthetic Aerosol Data Set - Analysis and Interpretation," Rougemont, North Carolina (3/16/82).

Currie, L. A., "Receptor Models, Isotopic Tracers, and Multidimensional Chemical Analysis," University of Alberta, Canada, (4/22/82).

Currie, L. A., "Miniature Signals and Miniature Counters: Accuracy Assurance via Microprocessors and Multiparameter Control Techniques," University of Washington, Seattle, Washington, (6/23/82).

Currie, L. A., "Anthropogenic Changes in Organic Carbon and Trace Metal Input to Lake Washington," University of Washington, Seattle, Washington, (6/22/82).

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Chabay, I. S., "The Bigger They Are, The Harder They Fall: Accurate Aerosol Size Measurements by Doppler-Shift Spectroscopy," American Association for Aerosol Research, Miramar Sheraton Hotel, Santa Monica, CA (2/19/82).

Etz, E. S., "Materials Characterization by Raman Microprobe Spectroscopy," Dept. of Analytical Chemistry and Failure Analysis, COMSAT Laboratories (12/17/82).

Etz, E. S., "A New Spectrograph with Multichannel Optical Detector for the Raman Characterization of Microparticles," Joint Meeting of Electron Microscopy, Society of America (EMSA) and the Microbeam Analysis Society (8/12/82).

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Fried, Alan., "Trace Detection of Atmospheric Molecules by Photothermal Techniques," Presented at IBM Research Labs, San Jose, Calf., (8/12/82). Invited

Fried, Alan., "Application of Photothermal Techniques for Trace Detection of NO_2 in the Troposphere," Presented at NASA's Instrumentation Workshop for $H_x O_y$ and $N_x O_y$ Tropospheric Species, (8/16-20/82) Palo Alto, Calf. Invited

Gerlach, R. W., "Description of Procedures for Generating Aerosol Data Set and Properties of the Data Set," Environmental Protection Agency, Quail Roost Conference Center, Rougemont, North Carolina (3/15/82).

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McKenzie, R. L., "Development and Characterization of Personal Samplers for Respirable Particulates and Gases," International Symposium on Indoor Air Pollution, Health and Energy Conservation, University of Massachusetts Amherst, Massachusetts (10/15/81).

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Newbury, D. E., "Beam Broadening in a Strongly Scattering Target in the Analytical Electron Microscope," Microbeam Analysis Society - Electron Microscopy Society of America Joint Conference (8/10/82).

Newbury, D. E., "Stereographic Presentation of Monte Carlo Electron Trajectory Simulation Results - Electron Microscopy, Society of America Joint Conference (8/13/82).

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Schmidt, W. P., "Development of SRM's Containing Selected Organic Vapors in Compressed Gas Mixtures," Environmental Monitoring Systems Lab. Environmental Protection Agency, Mission Valley Inn, Raleigh, NC (5/6/82).

Simons, D. S., "Isotopic Analysis with the Laser Microprobe Mass Analyzer (LAMMA)," American Society for Mass Spectrometry, Honolulu, Hawaii (6/9/82).

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Small, J. A., "Microprobe Analysis of Particles 0.05-10 μm in Diameter, University of Maryland Nuclear and Atmospheric Chemistry Division Seminar (1/29/82).

Small, J. A., "The Analysis of Asbestos Fibers by Analytical Electron Microscopy Development of Reference Filter Standards, Pittsburgh Conference (3/82).

3. Committee Assignments

Harry Rook
- 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
- Member, Office of Water Data Coordination, Committee 5F

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

David Bright
- Member, NBS Postdoctoral Selection Committee
- 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, International Committee for the Calibration of the Radiocarbon Time Scale
- Member, Model Validation Subcommittee - Receptor Modeling Workshop
- Member, CAC Computer Utilization Committee

William Dorko
- Member, American Chemical Society, Washington Section, Board of Managers

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

Robert Myklebust
- President Microbeam Analysis Society (National Council)
- Member, ASTM E-2 Emission Spectroscopy
- Member, ASTM E-2.04 Standard Reference Materials
- Chairman, Arrangements for 1982 MAS/EMSA National Meeting

Dale Newbury
- Chairman, Microbeam Analysis Society
- Chairman, Technical Program Committee
- Chairman, National Council for the MAS
- Member, ASTM E-42 Surface Analysis
- Member, Journal of Microscopy, Editorial Review Board
- Member, Scanning, 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_2 and Climate
    Member, Stratospheric Ozone Protection
    Member, Indoor Air Quality
    Member, ASTM D-22 Sampling and Analysis of Atmospheres

4. Other

a. Seninars

August 2, 1982	-	Prof. Georges Slodzian, Center de la Recherche Scientifique, Orsay, France, "Recent Advances in Instrumentation for Secondary Ion Microscopy,". (NBS Sponsor: D. Simons)
March 22, 1982	-	Prof. Jack Dodd, Hamilton, New York, "Schlieren Microscopy of Small Particles," (NBS Sponsor: H. Rook)
June 1, 1982	-	Permatina S. Goel, Department of Chemistry, Indian Institute of Technology, Kanpur, India, "Non-magnetic Origin of Iron Meterorites," (NBS Sponsor: L. Currie)
July 15, 1982	-	Prof. Richard Laub, Chemistry Department, Ohio State University, "How to Separate Almost Anything from Practically Everything Else," (NBS Sponsor: W. Zielinski)

b. Standard Reference Materials

<u>X-Ray Fluorescence</u>

1248C Alloy
1244 Alloy
1245 Alloy
1246 Alloy
1247 Alloy
C1285 Alloy
C1285A Alloy
C1137, C1137A Alloy

Gas Metrology Group

1625 SO_2 Permeation Tube, 10 cm
1626 SO_2 Permeation Tube, 5 cm
1627 SO_2 Permeation Tube, 2 cm

1629 NO_2 Permeation Tube

2653 NO_2/Air 250 ppm
2654 NO_2/Air 500 ppm
2655 NO_2/Air 1000 ppm
2656 NO_2/Air 2500 ppm

1683 NO/N_2 50 ppm
1684 NO/N_2 100 ppm
1685 NO/N_2 250 ppm
1686 NO/N_2 500 ppm
1687 NO/N_2 1000 ppm
2630 NO/N_2 1500 ppm
2631 NO/N_2 3000 ppm

1677 CO/N_2 10 ppm
1678 CO/N_2 50 ppm
1679 CO/N_2 100 ppm
1680 CO/N_2 500 ppm
1681 CO/N_2 1000 ppm

2612 CO/Air 10 ppm
2613 CO/Air 18 ppm
2614 CO/Air 42 ppm

1658 CH_4/Air 1 ppm
1659 CH_4/Air 10 ppm
1660 CH_4/C Hg/
Air 4 ppm CH_4 - 1 ppm C_3Hg

1661 SO_2/N_2 500 ppm
1662 SO_2/N_2 1000 ppm
1663 SO_2/N_2 1500 ppm
1664 SO_2/N_2 2500 ppm

2627 NO/N_2 5 ppm
2628 NO/N_2 10 ppm
2629 NO/N_2 20 ppm

1670 CO_2/Air 330 ppm
1671 CO_2/Air 340 ppm
1672 CO_2/Air 350 ppm

1911 Benzene Permeation Tube

1805 Benzene/$N_2$0.25 ppm
1806 Benzene/N_2 10 ppm

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

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, 1982 in the Laser Analytical Chemistry Group, 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, the National Environmental Specimen Bank, and service analysis coordination.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Analytical chemistry; analytical services; gas and particulate science; inorganic analytical chemistry; National Environmental Specimen Bank; organic analytical chemistry; quality assurance; voluntary standardization.

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