Dr. Reimann

Div. 550

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Annual Report 1981
Center for Analytical Chemistry

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

October 1980

Final

Issued December 1981

Prepared for
U.S. DEPARTMENT OF COMMERCE
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ANNUAL REPORT 1981
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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I. Center for Analytical Chemistry

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 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 impact 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.

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 measurement methods. 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 Instrumentation Development 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. Much work in progress is omitted but will be included in subsequent Annual Reports.

1. Outputs and Interactions

a. Publications

Reimann, C. W., Velapoldi, R. A., Hagan, L. B., Taylor, J. K., "Technical Activities 1980, Center for Analytical Chemistry", NBSIR 80-2164 (December 1980).

Taylor, J. K., "Quality Assurance of Chemical Measurements", Thalassia Jugoslavica 16 (2/3), 111-123 (1980).

Kratochvil, B. G. and Taylor, J. K., "Sampling for Chemical Analysis", Anal. Chem. 53, 924A-938A (1981).

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", accepted: J. Phys. Chem. (October 1981).

Reimann, C. W. and Uriano, G. A., "Letter to the Editor on Lead in Albacore: Guide to Lead Pollution in Americans", Science, in press.

Reimann, C. W., "Letter from America", European Spectroscopy News, in press.

b. Talks

J. K. Taylor, "Quality Assurance and Traceability", Pullman-Kellogg Company, Houston, TX, December, 1980.

J. K. Taylor, "Quality Assurance and the National Measurement System", 1981 Measurement Science Conference, Anaheim, CA, January 31, 1981.

C. W. Reimann, "Projections and Directions for Analytical Chemistry", American Chemical Society Meeting, New York, New York, August 27, 1981.

W. B. Crummett and J. K. Taylor, "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry", IUPAC International Symposium on Harmonization of Collaborative Studies, Helsinki, Finland. August 21, 1981.

c. Committee Assignments

Lucy B. Hagan
Member, ASTM D-5, Coal and Coke
Member, ASTM D-34, Waste Disposal
Member, CAC Committee on Computer Requirements

Curt W. Reimann
    Member, Regulatory Affairs Committee, American Chemical Society

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/SC1, 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
    Member, ASTM D19.02, General Specifications
        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 D22.07, Precision and Accuracy
        ASTM D22.09, USTAG to TC 146
        ASTM E34, Occupational Safety and Health
        ASTM E36, Criteria for the Evaluation of Testing & Inspection Laboratory
        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

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 Fluoresence Spectroscopy

d. Center Colloquium Series

November 12, 1980 - Typhoon Lee, Carnegie Institution, Washington, D.C. "Origin of the Chemical Elements: New Clues from High Precision Mass Spectrometry"

December 10 - Glen Gordon, University of Maryland, College Park, MD, "Receptor Models for Urban Atmospheric Particles"

January 14, 1981 - A. R. Findeis, National Science Foundation, "Analytical Chemistry Research: Options and Opportunities"

February 11 - Merle A. Evenson, University of Wisconsin, Madison, Wisconsin, "Prospectus for Analytical Chemistry in Clinical Analysis Laboratories"

April 15 - James G. Anderson, Harvard University, "Free Radicals in the Stratosphere: Measurement and Interpretation"

May 6 - Tomas Hirschfeld, University of California, Lawrence Livermore Laboratory, "Hyphenated Methods in Analytical Chemistry"

May 22 - G. J. Wasserburg, California Institute of Technology, "New Inferences on the Structure and Evolution of the Earth", Joint NBS and CAC Colloquium

B. Voluntary Standardization and Quality Assurance

1. Voluntary Standardization

Participation of the staff in the voluntary standardization process is recognized as providing important benefits. It furnishes:

- an important mechanism to transfer technology to the user public;
- a vital means of communication to learn the problems that confront the analytical community; and,
- a window to the state-of-the-art of analytical measurements as practiced in important applied situations.

Accordingly, standardization activities are an important part of the Center's external program and may be considered as one side of a coin which may be called scientific-technical interactions. The other side is, of course, the attendance at and participation in scientific organizations which provide direct contact with the science of analytical chemistry as it is developing.

Historically, the Center has a long involvement in standardization activities. The early staff participated actively in the highly industrially oriented committees of ASTM. In fact, such association provided the mechanism for much of the SRM development for the metals industry, for example. Tenures of 10 to 20 years on ASTM committees were not uncommon for such staff members.

As ASTM has extended its area of interest from a largely industrial orientation to include a wide variety of measurement problems, a number of new committees have been established. Many of these address problem areas in which the Center has become concerned, such as the environmental area. Center personnel have become involved in them at the expense of some diminution of effort in the industrial area.

Much of the national standardization activity has international parallelisms. Although several foreign countries' standardization programs are of long standing and are highly advanced, particularly those of France, Germany, and the United Kingdom, American standards are often believed to be the best and/or need to be promoted for international adoption, in the interest of facilitating U.S. commercial interests. Prestigious analytical chemists, highly knowledgeable of American standards, can be very influential to this end. Accordingly, several Center scientists have become very active in international standardization activities and have assumed positions of leadership which have proven to be beneficial to U.S. standardization interests.

There are many parallels in the area of purely scientific standards. Center chemists have long been involved in the important activities of standardizing atomic weights and compiling electrochemical data, in particular. They have not only personally made contributions to the determination of physical constants that need to be promoted for adoption, but they often have a keener feeling for the importance of accuracy in chemical measurement than many of their counterparts on the committees. When highly knowledgeable chemists reinforced by the prestige of NBS are the U.S. representatives on such committees, the interests of U.S. science are well represented. Accordingly, such participation needs to be encouraged and supported.

The present standardization participation of CAC personnel may be classified in two general categories:

- Active - attendance at meetings; participation in writing standards; leadership
- Passive - participation by correspondence; review of standards

The statistics are as follows:

- 31 members (approximately 37% of full-time professional staff) participate in standardization activities
- representation on 109 separate committees, subcommittees, or task groups
- ASTM participation is the largest
    - 11 ASTM Committees
    - 71 Subgroups
- representation on 12 international committees

One further activity of standardization needs to be mentioned. This is concerned with participation in collaborative testing of proposed standards. Sometimes specific technical points need to be investigated by a peer laboratory. The CAC is often exceptionally well qualified to provide such a service. There is also the need to actively participate in the actual collaborative tests. A related matter is the provision of test samples for such tests. The Center's expertise in SRM development and certification knows no peer in this respect and the furnishing of test samples, as possible, is a major contribution, often eliminating an impossible roadblock.

2. Quality Assurance

The quality assurance tempo has increased considerably during the past year. A formal quality assurance plan for both the research and applied analytical measurements programs of the Center has been developed for expected implementation next year. In addition, assistance has been provided in the writing of quality assurance plans for the Office of Standard Reference Materials and for the Office of Environmental Measurements. The Center, of course, is a major contributor to both of these program areas; hence, it is important that all of the quality assurance plans be compatible.

The quality assurance plan developed formalizes the measurement practices developed over the years, as the Center has strived to provide the best analytical measurements possible, especially for reference material certification. The policy with respect to sampling, analytical methodology, laboratory records, and data review and reporting is described in some detail. It affirms the importance of maintaining control charts and the present policy of data verification by use of multiple techniques, multiple operators, replicate measurements, and the systematic use of SRM's and other reference materials for quality assessment. The dependence of quality data on planned experimentation, backed by statistical advice, is emphasized. Copies of the plan are available on request to others who may wish to consult it with respect to developing or revising their own quality assurance plans.

As part of the Center's program to assist the technical community by encouragement of quality assurance and good measurement practices, the first NBS Precision Measurement Seminar in the chemical area was organized and held May 7-8, 1981. The seminar, "Quality Assurance of Chemical Measurements" is a two-day seminar concerned with techniques to improve the precision and accuracy of analytical measurements such as those needed in the compositional analysis of materials, process control, and regulatory enforcement. It is designed for supervisors of analytical laboratories, experienced analytical chemists, and those responsible for the development and/or supervision of laboratory quality control programs. The seminar consists of in-depth discussions of the following topics: general aspects of quality assurance; the role of Standard Reference Materials in quality assurance; statistical considerations used in the evaluation of data quality; good laboratory practices for precise and accurate chemical measurements. An additional feature is small-group discussions of good measurement practices (GMP) for selective measurement techniques with NBS experts. Each participant elects to participate in 3 of these, selecting from the following areas: atomic absorption spectrometry; gas analysis; gas chromatography; gas chromatography-mass spectrometry; general analytical chemistry; ICP spectroscopy; ion chromatography; isotope dilution mass spectrometry; liquid chromatography; polarography-voltammetry; neutron activation analysis; spectrophotometry; statistical concepts; UV-IR organic spectroscopy; standard reference materials; quality assurance program development.

Twenty persons, largely from industry, attended the first seminar. Four such seminars are scheduled to be held on December 1-2, 1981, May 4-5, May 6-7, and May 13-14, 1982, respectively.

A series of quality assurance seminars for Center personnel, but also attended by other staff members of NBS and to some extent from other government agencies, was held during the past year. This lecture series is designed to inform the Center of quality assurance practices and needs of the analytical community and also to provide a means to present discussions of specific techniques by experts in the field. The seminar series will continue during the coming year. The list of subjects of the previous seminars is given below.

Quality Assurance Seminar Series

Feb. 18, 1981	Robert Belfit, Dow Chemical Company, "Methods and Standards at the Dow Chemical Company"
March 23, 1981	J. Stuart Hunter, Princeton University, "A Statistical Look at Calibration Uncertainties"
April 30, 1981	Byron G. Kratochvil, University of Alberta, "Sampling for Chemical Analysis"
May 26, 1981	Dexter Olsson, Bethlehem Steel Corporation, "Quality Assurance Practices in the Steel Industry"

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 relating to the establishment of a National Environmental Specimen Bank. The purpose of such a national system would be (1) to detect changes in the environment, using bioaccumulators as indicators, on a real-time basis (i.e., monitoring), (2) to distinguish such changes from natural inputs, and (3) to provide a "bank" of samples for retrospective analyses in future years as analytical techniques improve or as new pollutants are identified. In 1979, a special "clean" laboratory/storage facility was completed at NBS to initiate a five-year Pilot National Environmental Specimen Bank Program. This pilot program is designed to evaluate the feasibility of a national program by: (1) developing analytical protocols for sampling, processing, and storage of four types of environmental samples (i.e., human liver, mussels, grain/milk, and air filters/ moss/lichen); (2) evaluating and improving analytical methods for the determination of both trace element and organic pollutants in biological matrices; (3) evaluating the feasibility of long-term storage at various conditions; and (4) providing a "bank" of valid samples for retrospective analyses in future years.

During the past year, several important accomplishments have been achieved: (1) completion of the first-year human liver sample collection and evaluation of the liver sampling protocol; (2) improvements in development, evaluation, and application of a cryogenic homogenization technique for biological samples; (3) analyses of 36 liver samples for trace elements by several analytical techniques; (4) development of analytical methodology for organochlorine pesticides in human liver samples; (5) development of a liquid chromatographic/amperometric detection method for the determination of methylmercury in human livers and mussels; (6) development of a neutron activation analysis procedure for the determination of platinum; and (7) development of a sample collection and storage protocol for the marine bivalve sample, mussels.

2. Sample Collection

During the first year, 300 liver samples from three geographical locations were collected using the sampling protocol developed at NBS. During the remaining years of the pilot study, liver samples will be received at a reduced rate of approximately 100 per year because of financial/manpower constraints. At the completion of the first year of human liver collection, the sample collection protocol and strategy were evaluated with respect to such items as: initial set-up cost for contractors; sample procurement costs (i.e., contractors' cost, protocol materials, and shipping), transport time, time required for receipt of hepatitis screening results and histological slides, and suitability of donor selection criteria. Regarding donor selection criteria, one contractor summarized the total cases available for sampling, types of cases, number of cases (donors) rejected, and reasons for rejection. This contractor reported that the major factor for rejection was the time requirement that the autopsy be performed within 24 hours of death. The most likely sources of liver samples for this contractor were found to be

(1) natural deaths, (2) suicides, and (3) traffic accidents. Legal constraints prevented the use of any tissue from a probable homicide case in that particular state. However, homicide cases provided a major source of samples for a contractor in another state where such legal restrictions do not exist. Information and experience as described above for the liver sampling protocol will be used to evaluate the feasibility (i.e., costs, legal aspects, sampling difficulties, etc.) of initiating a National Environmental Specimen Bank Program.

3. Sample Preparation and Analysis

Specimen banking, as part of biological monitoring efforts, includes the important task of developing and establishing a credible analytical measurement system. Each type of specimen considered for monitoring and banking places certain demands on a measurement system; hence, the measurement capabilities should be developed in conjunction with the design and implementation of a banking program.

An important part of the first phase of the pilot program, i.e., the banking of human liver specimens, has been the development of a state-of-the-art protocol for the chemical analysis of these specimens. Research efforts in CAC have resulted in the currently applied analytical protocol which covers three major areas: (1) the preparation of the sample for analysis, i.e., subsampling to obtain a representative analytical test portion; (2) the implementation of a comprehensive inorganic analytical scheme, which is suitable to provide credible results for all aspects of specimen banking studied in the pilot program; and (3) the evaluation of methods and procedures for selected organic pollutants.

The pilot program and possibly any biomonitoring and banking program has to operate under certain constraints regarding the amount of material available from which the desired set of data must be obtained. The analytical increment must be representative of the sample and be homogeneous for subsampling of the analytical test portions on which the results are based. Sample preparation research has focused on the expansion of the cryogenic brittle fracture technique to sample sizes up to 250 g. To allow a one-step, contamination-free homogenization of the analytical increment, i.e., half a left lobe of a human liver, a Teflon disk mill has been designed at NBS, and its performance evaluated. (See page 51 for detailed discussion of this evaluation.) Ingamells' sampling constant, K_s, has been determined by radiotracer experiments, showing that test portions of one gram of fresh liver provide a sampling uncertainty of less than one percent. More homogeneous samples allow detection of smaller changes in concentrations during the storage evaluation and/or the use of smaller test portions which allows multiple analyses of the same sample.

Research in trace element analysis has resulted in the improvement of existing methods and the development of new procedures emphasizing higher sensitivity for many of the elements. The result is an analytical protocol which includes the determination of most of the first-priority elements proposed by the 1978 International Workshop on Monitoring Environmental Materials and Specimen Banking [1]. Other elements regarded as possible pollutants have been added to the protocol, as well as biological major elements and trace elements, which can provide information about the "normal" state of the specimen. The analytical protocol includes about 40 elements, which are determined by the following methods: atomic absorption spectrometry (AAS), isotope dilution mass spectrometry (ID/MS), neutron activation analysis (NAA), and voltammetry (VOLT). The specific elements determined and the analytical techniques employed for each measurement are summarized in figure 1. The analytical protocol was applied to the analysis of 36 liver specimens collected during the first year of the pilot program. The quality assurance procedures include parallel determinations of Standard Reference Materials, determination of several elements by more than one technique, and use of high precision, high accuracy techniques, e.g., ID/MS.

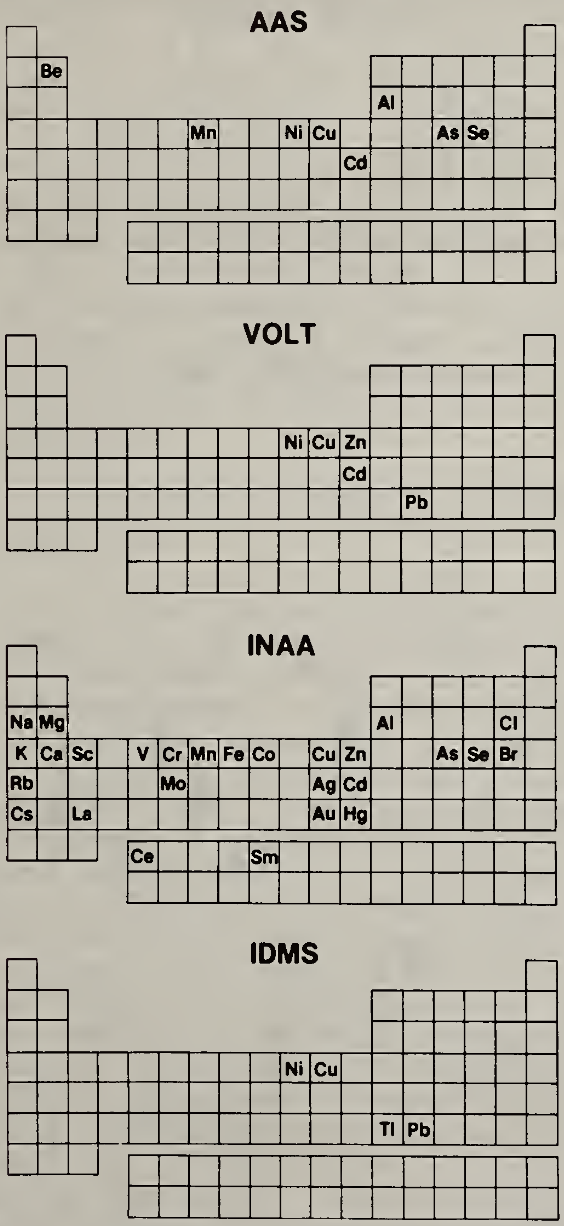

Figure 1. Analytical techniques used for the determination of trace elements in human liver samples.

AAS, NAA, and VOLT provided precise and accurate results for the majority of the elements of interest. The relative standard deviation of repetitive analyses using these methods varied between 1 and 7 percent with the exception of the determination of Al, Cd, and Pb, where the precision ranged from 10 to 15 percent. ID/MS provided accurate and precise data (∿1 percent error) on Cu, Tl, and Pb. For the evaluation of storage conditions, a relative standard deviation of 5 percent or less is essential to detect changes smaller than 10 percent. Some important elements, e.g., Be and Ni, are at or below the detection limits of the currently applied analytical procedures; research will be directed to develop the needed methodology for these elements. Determination of elements by more than one method illustrates the high degree of accuracy achieved with the applied protocol. Data on Al, Cl, K, Mn, and Se agree among the methods. The results of the multielement determinations of the 36 liver specimens are shown in figure 2. The concentrations agree with the ranges reported previously [2,3]. Of particular interest is the very narrow concentration spread of some of the essential trace elements, especially selenium, when compared to the widely scattered concentrations of non-essential or pollutant elements. These results will contribute significantly to the existing trace element data base for human livers. For the purpose of biomonitoring and specimen banking, the data obtained during the first phase of the pilot program indicate that the analysis of individual specimens is preferable to the analysis of a large composite of several livers. Results based on individual specimens may provide a more realistic picture of pollutant levels, since high levels in single individuals may be uncharacteristic for the sampled population because of specific circumstances.

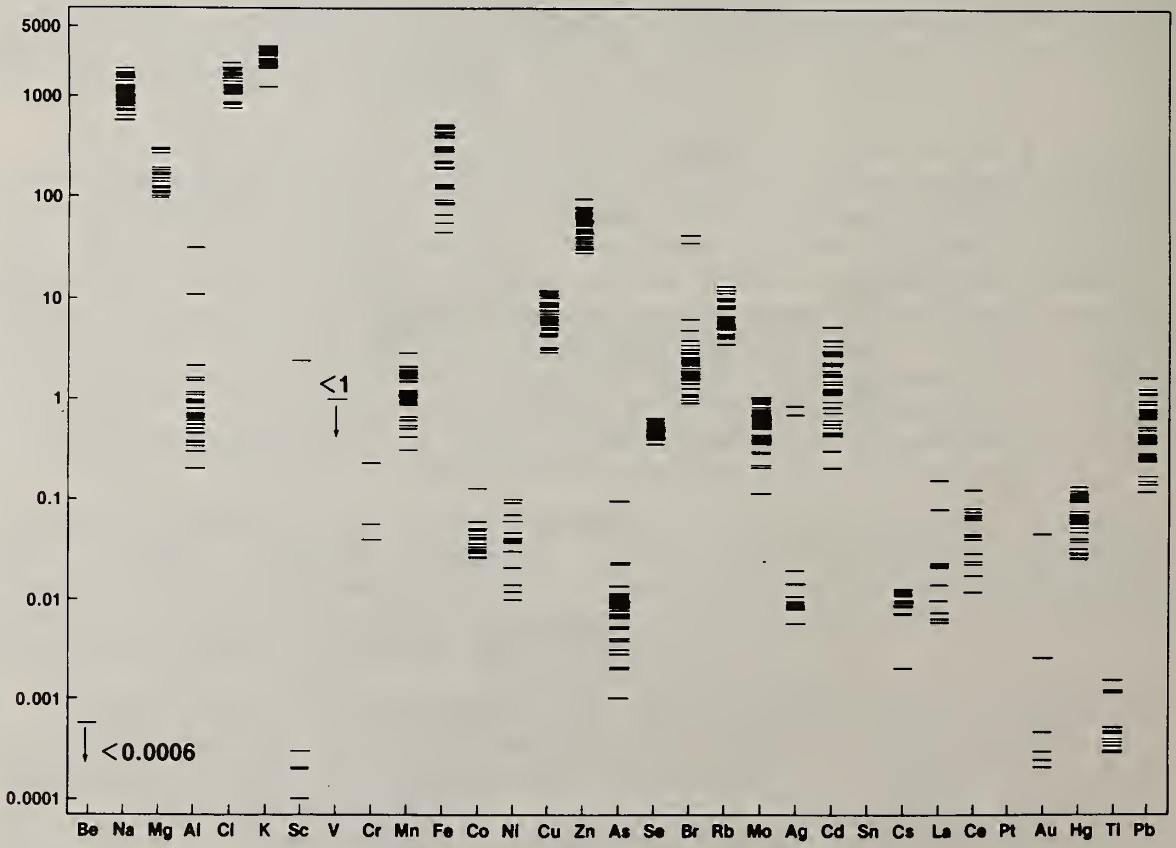

Figure 2. Elemental concentrations (µg/g) determined in 36 liver specimens.

Analytical methodology for the determination of organochlorine pesticides has been developed and applied to several liver samples. The major chlorinated compound in each sample was identified as p,p'-DDE (a metabolite of DDT) by gas chromatography (GC) and mass spectrometry (MS). This compound was determined in three different samples using both GC and GC/MS. The results of these analyses are summarized in Table 1. Table 1 also includes the result of an interlaboratory sample split with the U.S. EPA Health Effects Research Laboratory. Trace quantities (∿10-100 times less than p,p'-DDE) of hexachlorobenzene, β-hexachlorocyclohexane, oxychlordane, hepachlor epoxide, *trans*-nonochlor, and dieldrin have also been found. This methodology will be applied for the analysis of ∿30 liver samples during the coming year.

Table 1. Determination of p,p'-DDE in Human Livers.
(μg/g wet weight)

Sample I.D.	GC[a]	GC/MS	GC (EPA)[d]
B0025	A. 0.72 ± 0.04	0.77[b]	
	B. 0.75 ± 0.04	0.81[b]	
M0136	0.23 ± 0.01	0.23[c]	0.26
S0129	0.35 ± 0.01	---	

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[a] Uncertainty based on four determinations, reported as one standard deviation from the mean.

[b] Single determinations.

[c] Mean of two determinations, range of ±7 percent.

[d] Single determination.

Recent research on the determination of additional pollutants has resulted in the development of an NAA procedure for the determination of platinum and a liquid chromatographic procedure with amperometric detection for the determination of methylmercury. The NAA procedure via radiochemical separation techniques is capable of measuring platinum at naturally occurring levels of 5 x 10^{-11} g/g in human livers, thus providing the first baseline data for this element in human liver. The procedure for the determination of platinum is described in detail in another section of this report. Of the various forms of mercury, which has long been recognized as an important environmental pollutant, the alkyl mercury cations have been found to be the most toxic. Thus, the determination of the levels of various organomercury species in biological tissues is important in addition to the measurement of the total mercury concentration. As an alternative to time-consuming gas chromatographic methods which involve chemical derivatization for the determination of methylmercury in tissue samples, a simplified procedure based on liquid chromatography (LC) with amperometric detection has been developed. This method consists of (1) acidification to liberate the organomercury cations bound to the proteins, (2) complexation with a mercaptan, (3) followed by LC separation of methyl-, ethyl-, and inorganic mercury with amperometric detection to achieve the necessary selectivity. Research is in progress to improve the recovery of the various mercury species, particularly the inorganic mercury(II), to achieve simultaneous determination of all of the expected forms of mercury in tissue.

4. Mussel Protocols

The second type of environmental sample for incorporation into the pilot program will be 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. The cryogenic homogenization technique has also been evaluated for use with mussel samples and will be modified to accommodate larger sample sizes.

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, e.g., how many mussels constitute a sample, what is the variability between "pools" of 50-100 mussels from the same site, and should the mussels be stored in the shell, shucked, or as homogenates? The sampling and storage evaluation strategies were designed, in cooperation with NBS statisticians, to address these questions. Initially, sample collection will be directed at one site to determine the expected "variability" of "pools" of mussels. These data will then be used to evaluate the probability of detecting changes during the storage of mussel samples. Several sites (both polluted and unpolluted) will be evaluated in a similar manner in the future. Currently, we are developing analytical methods for the measurement of both trace elements and trace organics (i.e., organochlorine pesticides and polycyclic aromatic hydrocarbons) in these "pooled" mussel samples.

5. Interactions with National and International Programs

Since 1975, the U.S. EPA and the Environmental Agency of the Federal Republic of Germany (FRG) have been pursuing collaborative research in the area of environmental specimen banking as part of a bilateral agreement on the environment. Participants in the specimen banking programs of the U.S. and the FRG meet annually to exchange information and experience. As a result of these meetings, for example, participants in the FRG program provided NBS with their methodology for extraction/isolation of organochlorine pesticides from liver samples. This methodology has been incorporated into the NBS program. Information concerning the formatting of data/sample information has been exchanged to make the results of the two programs intercomparable. The FRG program is currently investigating the use of cryogenic homogenization patterned after the work at NBS. These are several areas where the U.S. and FRG programs have exchanged information/experience for the benefit of both programs. In May 1981, NBS scientists attended the annual meeting in Jülich, Germany, and reported the research activities of the pilot program. This meeting was held in conjunction with the dedication of the Pilot Environmental Specimen Bank facility for the FRG. At this meeting, several sample splits were arranged between the two programs (i.e., liver samples from both programs and a human blood reference material from the FRG program). An additional interlaboratory comparison for the determination of methylmercury was planned for early 1982.

The U.S., through the NBS/EPA Pilot National Environmental Specimen Bank Program, is looked upon as a leader in specimen bank research. NBS representatives have been invited to prepare two position papers for the "International Workshop on Environmental Specimen Banking and Monitoring as Related to Banking" to be held in May 1982 in Saarbrücken, Germany.

As a result of NBS specimen banking activities with human livers, NBS researchers have also been invited to participate in a select panel concerning "Collection and Preservation of Samples" and "Analytical Methodology" for a follow-up meeting to the "Workshop on Research Needed to Improve Data on Mineral Content of Human Tissue," which was sponsored by the American Institute of Nutrition and the National Science Foundation. The goal of this upcoming workshop, entitled "Protocols--Mineral/Element Analysis of Human Tissues," is to prepare specific protocols for sample collection, preservation, and analyses of human tissues.

References

[1] N.-P. Leupke, editor, Monitoring Environmental Materials and Specimen Banking, Martinus Nÿhoff, The Hague-Boston-London (1979).

[2] G. V. Iyengar, W. E. Kollmer, and H. J. M. Bowers, The Elemental Composition of Human Tissue and Body Fluids, Verlag Chemie, Weinheim-New York (1978).

[3] S. H. Harrison, R. Zeisler, and S. A. Wise, Pilot Program for the National Environmental Specimen Bank - Phase I, EPA Research Report, in press.

S. A. Wise, Project Manager; K. A. Fitzpatrick, S. H. Harrison, R. L. Zeisler

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

S. N. Chesler, R. R. Greenberg, L. R. Hilpert, W. F. Kline, B. Kratochvil, J. K. Langland, W. A. MacCrehan, E. J. Maienthal, T. J. Murphy, P. A. Pella, L. P. Powell, T. C. Rains, T. A. Rush, R. L. Watters.

D. Service Analysis

An accepted and important function of the Center for Analytical Chemistry is the provision of consultation, advice, and accurate chemical analyses on the diverse materials that are utilized in the research programs at NBS. This service is also available to other federal, state, and local government agencies on request. In addition, in special instances where CAC has a unique analytical capability, this service is likewise extended to the private sector.

In the performance of the service analysis function, every member of the CAC staff is dedicated to providing informative, timely, and cost effective analyses. At the same time, an extensive effort is made to provide this function with a minimum of disruption to ongoing programs within the Center. The turnaround time for the more straightforward analyses typically ranges from several days to about two weeks. All work is performed on a cost reimbursable basis. Within NBS, funds are transferred by means of an inter-division work order; outside work is handled on a purchase order.

In FY 81, some 134 service analyses were performed within the Center at a cost of $181K. These were distributed among the three types of customers as follows: NBS, 51 requests ($38,000); other government agencies, 20 requests ($44,800); and private industry, 63 requests ($97,800). More than half of the industry requests were in two areas, recalibration of glass transmittance standards and recertification of gas mixtures.

Of the service analyses carried out in FY 81, two stand out as good examples of the kind of analytical services performed and the value that can be derived from them. One was concerned with a problem of a decrease in the temperature coefficient in platinum resistance thermometers. The other analysis involved a new type of superconductor material and required the development of a new analytical method.

An important program within the Temperature and Pressure Measurements and Standards Division of the Center for Absolute Physical Quantities involves the development of high temperature platinum resistance thermometers suitable for use as interpolating instruments to the gold point on a revised international practical temperature scale. Many of the thermometers made during the past year have undergone an unexpected decrease in temperature coefficient upon prolonged exposure to high temperature (1100 °C). In an effort to trace potential causes for this decrease, CAC was requested to analyze some of the thermometer components.

The first analyses, by arc emission spectrometry, of samples of platinum taken from the resistance elements of two thermometers revealed the presence of copper, an unexpected contaminant, at about the 200 ppm level. Subsequently, samples of all platinum materials were analyzed similarly, and samples of all fused silica materials used in thermometer construction were analyzed by neutron activation analysis. Some of the less pure platinum used for thermometer leads and general structures was found to contain appreciable amounts of copper; the fused silica, considered to be an unlikely source of copper contamination, was found to be essentially copper free. As a result of these analyses, a higher grade platinum is being substituted for the lead and ground structures and all external processing equipment is being examined for possible sources of copper contamination.

The other service analysis, performed for the Ceramics, Glass, and Solid State Science Division, entailed the measurement of the chloride concentrations in a series of specially prepared cadmium sulfide samples. Interest in cadmium sulfide, doped with chloride, is increasing because this material exhibits potentially superconductor-like properties at temperatures that are well above the cryogenic level. To provide the desired measurements, a procedure was developed in which the samples were dissolved in alkaline hydrogen peroxide and analyzed by ion chromatography. It was also possible to determine sulfur in the same samples because the dissolution procedure quantitatively converts sulfide to sulfate, an anion that is easily measureable by ion chromatography. The chloride and sulfate data were subsequently used to calculate and demonstrate mass balance. A summary of this work has been submitted by W. F. Koch and J. W. Stolz for publication in Analytical Chemistry.

R. W. Burke

E. Instrument Development Group (proposed name: New Analytical Techniques Group)

1. Group Overview

The main objective of the group is to develop new approaches to performing accurate chemical analyses. The focal point continues to be the use of laser radiation in two ways. First, the inherent high power, time and space coherence, and spectral purity of laser radiation are attributes that lead to highly accurate spectroscopic analytical methods. Second, laser radiation is proving to be a powerful diagnostic tool for studying plasmas of analytical significance (e.g., the solution aspirated flame used in atomic absorption, fluorescence, or emission).

Major progress has been made this past year in the areas of IR diode laser instrumentation development and two color laser enhanced ionization (LEI) in flames. In the first area, the IR laser diode system was completely redesigned and was put under computer control. It shows greatly improved reliability and provides compensation for some instabilities observed in the operation of the diode itself. In the second area, two-color LEI in flames, we have acquired a Nd-YAG laser to act as a pump for one dye laser head and borrowed a second dye laser. This system allows the population of high atomic energy levels that were unreachable with a single dye laser. With the two wavelength system, elements have been analyzed with high selectivity and with detection limits at the 10-100 pg/mL level, both of which imply a highly accurate, trace analytical, spectroscopic technique. The reliability of the system is excellent and there appears to be no impediment to the use of this laser in routine analytical systems.

The first major paper on the LEI signal collection mechanism will soon be published in the Journal of Physical Chemistry. This paper incorporates much of the imaging data discussed in last years annual report. In research this year, we have observed a significant bleaching of ground state atoms in the laser beam. A mapping in two dimensions of the depleted area has been carried out as a function of time so as to make an interesting, time-lapsed "movie" of the phenomenon. A number of properties of flames can be studied by these techniques (diffusion, ion-electron recombination, and chemical reaction rates).

Collaboration with scientists in the other divisions is proceeding and several of the projects that are being worked on jointly are reported in other sections of this report. These include the organic molecular ion fragmentation studies in Division 552, the N_2O SRM gas analysis in Division 553, and the mass spectroscopy source diagnostic studies and ion beam fluorescence studies in Division 551.

Implementation of the NBS storeroom microcomputer system is proceeding well. The software is becoming powerful with convenient file managers, editors and applications languages becoming available at an ever increasing rate for use with the operating system called CP/M. These systems must be rated significantly more powerful per-dollar-invested than even the most economical minicomputer or desk calculator on the market. On an absolute scale of computing power, the system ranks near the middle of the minicomputer market.

Our general plans in the laser enhanced ionization area are to study the signal collection processes over short time intervals and to attempt to model mathematically the dynamic process of ion/electron transport over these time frames. Our collaborative efforts within the Center will continue to focus on multiphoton atomic-ionization and organic molecular fragmentation processes. Considerable attention has been placed upon new atom reservoirs. A new competence building program involving sample transport mechanisms has been proposed. Sample transport concerns the study of fundamental processes involved in removing analyte atoms from the sample and putting them into the form best suited for quantitative analysis (see section on new competence proposals). Collaboration on flame diagnostic studies outside of the Center will continue, but at a reduced pace because of insufficient staffing. Finally, of great importance, is our plan to characterize the LEI two-color excitation spectrum of the elements and to analyze an increasing number of materials to confirm our expectations that the LEI in flames is a viable analytical method for most of the elements.

James R. DeVoe

2. Selected Technical Accomplishments

a. High Reproducibility Analysis with the Infrared Diode Laser

The narrow linewidth and moderately high intensity of infrared semiconductor diode lasers (of the $Pb_{1-x}Sn_xTe$ type) provide an ideal radiation source for IR spectrophotometric analysis. Moreover, of the possible techniques that could be used (e.g., Fourier transform infrared spectroscopy, optoacoustic techniques), the laser diode system shows outstanding promise for making highly accurate and reproducible measurements. If high reproducibility can be realized, then analysis of Standard Reference Materials (SRM's) using comparative methods and the measurement of isotope ratios of, for example, carbon or nitrogen in small molecular gaseous species, becomes feasible and it also may be able to compete with classical mass spectrometric techniques. In addition, the narrow linewidth removes much of the interference due to line overlap from other species so that the measurement should be accurate. To obtain the necessary reproducibility, major changes were made to the diode system. These changes were a redesign of the optics and the entire electronic detection system.

Superimposed sinusoidal ripples in the spectral baseline coming from combined orders of various etalons unintentionally introduced via the lens system were observed. The optical lenses of the system were replaced by off-axis parabolic mirrors (see figure 3) which substantially reduced this instability.

Another source of optical instability results from a very small change in the geometric position of the laser beam with time. Since it is desirable to use small surface radiation detectors to minimize the magnitude of background signal and its accompanying noise, this positional instability moves

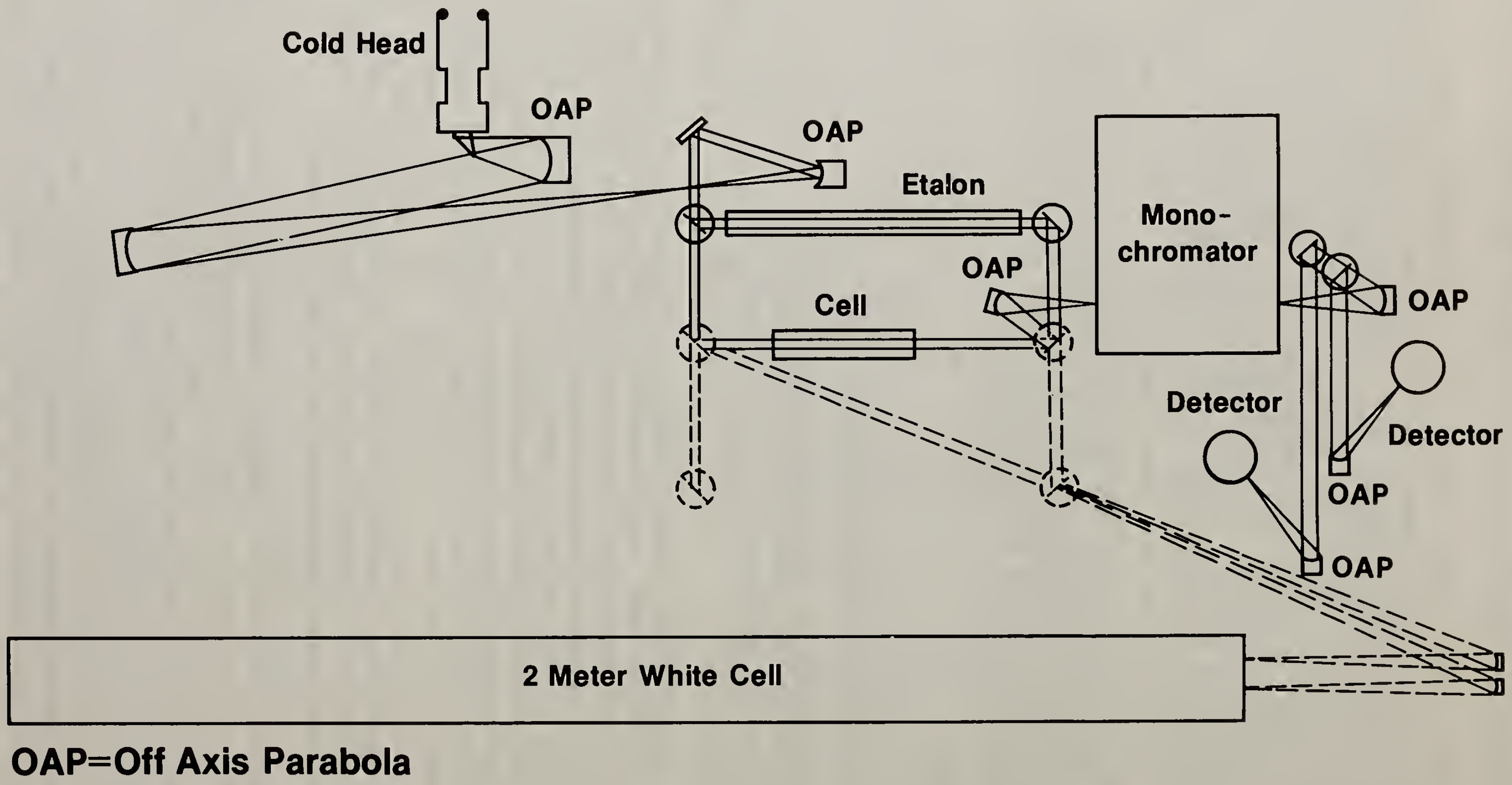


Figure 3. Diode laser optical system.

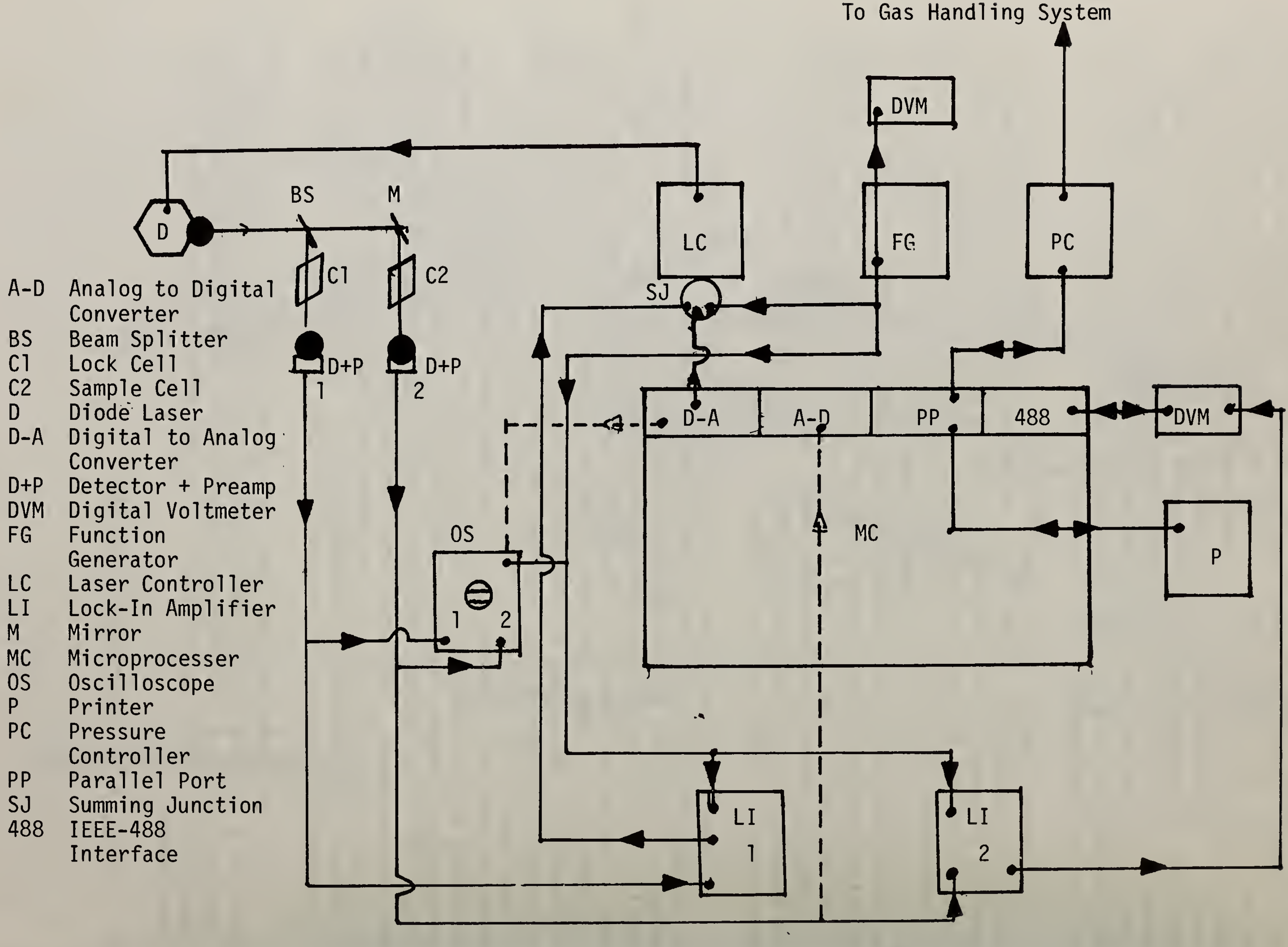
the IR beam on the detector surface, thereby causing intensity fluctuations. This spatial instability comes from two sources. One is from inconsistencies in the solid state properties of the diode, thereby causing a specific lasing mode to move to a position of optimal power output on the face of the diode crystal. The second source is dimensional instability of the optical components due to temperature fluctuations and building vibration. The former instability is under study. Its time response is slow so that adequate computer control may be able to reduce this effect. The latter instability was improved by installation of a thermal curtain and ruggedized supports for the optical components.

The above instabilities, coupled with diode dependent frequency and intensity fluctuations in the laser radiation plus background fluctuations, required a change in the philosophy of the entire operation of the system. A variety of modes of operation were desired and this is best done by computer. A storeroom microprocessor system was assembled (see description in Section E.2.e of this report). The computer sends an analog signal to the current amplifier which sets the frequency (wavelength) of the diode. The infrared detector's analog signal is digitized and stored by the computer. A number of system control routines have already been written and more are required. To date, a spectrum averager mode which sweeps at the maximum rate of 160 μs per wavelength unit has been completed. A jump scanning mode is also in operation including graphical display of data on a CRT.

In order to discriminate from background as well as to remove certain noise contributions, wavelength modulation is used in several operational modes. In addition to the sequential wavelength scanning and averaging, modulation is used to maintain frequency stability of the laser. Part of the beam is extracted through an absorption cell containing pure analyte gas. The wavelength is then modulated using an external signal generator at kHz frequencies. The output of the detector is locked to this frequency using the usual first derivative technique and any difference signal is fed to the current amplifier — control circuit. The primary gas sample system's detector goes to a similar lock-in and the second derivative spectrum is collected by the computer (see schematic, figure 4). Using this procedure and repeatedly measuring the second derivative output, a stability of 0.08 percent relative standard deviation (RSD) of the average of 500 measurements has been achieved. Long term stability over several hours decreased to about 0.1 percent RSD. In summary, the above improvements have provided at least a factor of ten increase in reproducibility. This technique has been used to measure N_2O samples (see report in Section IV. B.12).

It is believed that the stability of the system can be further improved by using a detector with a greater signal-to-noise ratio. However, the limiting factor on stability now appears to be in gas handling and pressure measurements. These operations will be put under computer control in the near future.

R. L. Sams, J. W. Elkins (Division 553)



A-D	Analog to Digital Converter
BS	Beam Splitter
C1	Lock Cell
C2	Sample Cell
D	Diode Laser
D-A	Digital to Analog Converter
D+P	Detector + Preamp
DVM	Digital Voltmeter
FG	Function Generator
LC	Laser Controller
LI	Lock-In Amplifier
M	Mirror
MC	Microprocesser
OS	Oscilloscope
P	Printer
PC	Pressure Controller
PP	Parallel Port
SJ	Summing Junction
488	IEEE-488 Interface

Figure 4. Electronic schematic for diode laser.

b. LEI Ion Collection Dynamics

When electrons and ions are produced in a flame by laser enhanced ionization, 10^{-6} - 10^{-4} s are required to transport the charged species through the flame by an electric field for collection on an electrode. For this reason, a steady state condition for the extraction of LEI-generated electrons and ions only exists for laser excitation lasting $>>10^{-6}$ s. Transient behavior showing a two-component (bimodal) current pulse with a 10^{-6} s flashlamp-pumped dye laser was the original inspiration for the post-doctoral proposal [1]. Since then, the phenomenon has been observed with better time resolution using $\sim 10^{-8}$ s laser pulses [2,3]. It is suspected that the bimodal signal observed with $\leq 10^{-6}$ s excitation is due to a very fast signal corresponding to electron movement which tracks the laser intensity, and a slower pulse which results from ion migration. In the continuous wave (CW) regime, a signal that is a combination of both electrons and ions is observed.

As described in previous panel reports, the addition of an easily ionizable species to the flame produces ions that migrate to the cathode, thereby causing a sheathing or passivation of the electric field produced by the signal collecting electrodes. With a water cooled cathode in the flame above the burner base which is the anode, significantly different behavior is observed between the use of a pulsed laser and a CW laser (figure 5). A simplified explanation relates to the experimental results described in the first paragraph above. With the pulsed laser, the detection circuit is gated to measure only the electron signal that occurs simultaneously with the laser pulse and a signal will be observed only when the laser irradiates the sheath region. No signal is observed if the pulsed laser is directed in the field free region (outside the sheath) because the electrons penetrate the sheath well after the measurement period. With CW laser irradiation on the other hand, a reasonably constant signal is observed independent of field and thus laser beam position. This is a consequence of "steady state" conditions in which electron-ion transit times are inconsequential, i.e., charges carried by large fields or at flame flow velocities are indistinguishable with the chopping frequencies used. This implies that matrix interferences of easily ionizable species in the flame can be significantly reduced by using CW lasers and the geometry with the cathode immersed in the flame.

Detection limits using the CW laser system were measured for potassium and rubidium. The limits of detection (LOD) are defined as the species concentration in water solution which gives a signal amplitude three times that of the blank noise level. A krypton ion laser was used to pump oxazine 725 dye. The limit of detection for potassium at an excitation wavelength of 776.5 nm was 100 pg/mL and the LOD for rubidium at 780 nm excitation was 90 pg/mL. A calibration curve was linear over four orders of magnitude. The insensitivity of this method to matrix effects caused by samples with easily ionizable elements was demonstrated by determining Rb in pine needles (SRM No. 1575) using aqueous solutions for calibration. A measured concentration of 11.1 µg/g ± 0.5 µg/g agreed well with the reported amount of 11.6 µg/g ± 0.1 µg/g. (The value ±0.5 µg/g is the standard deviation of a single determination excluding reproducibility for sample weighing and solution preparation. The value ±0.1 µg/g is that appearing on the certificate of analysis.)

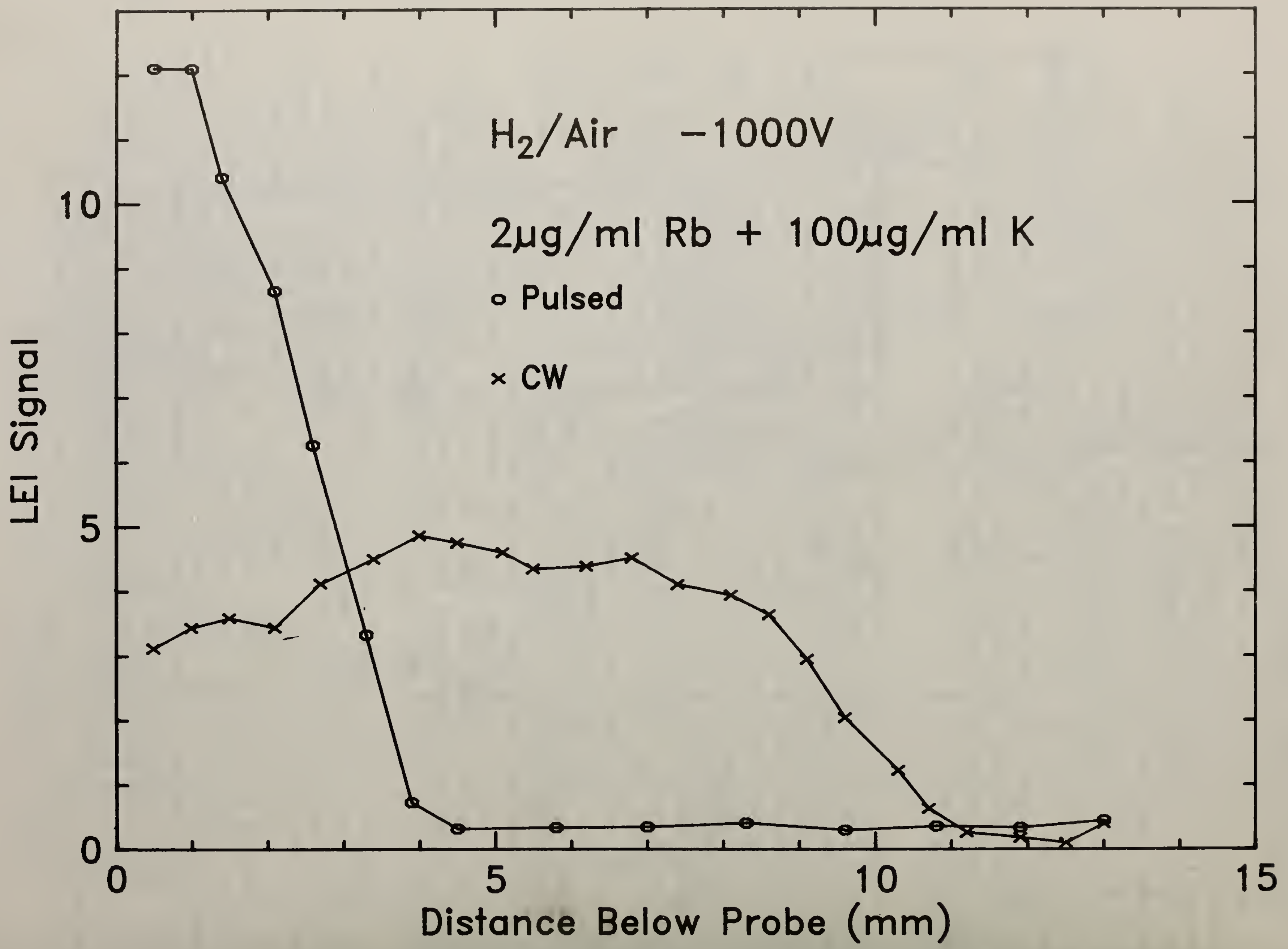


Figure 5. Plot of LEI signal vs. distance of the laser beam below the water cooled cathode immersed in the flame for a pulsed laser o and a CW laser x. The pulsed laser was a Chromatix CMX-4, pumping Rhodamine 640 dye at 629 nm.

References

[1] Havrilla, G. J. NAS/NRC Postdoctoral Research Proposal (1980).

[2] Mallard, W. G.; Smyth, K. C. Combustion and Flame, in press (1981).

[3] Turk, G. C. Anal. Chem. 53: 1187-1190; 1981.

G. J. Havrilla, J. C. Travis

c. Stepwise Excitation Laser Enhanced Ionization Spectrometry

Laser stepwise excitation, utilizing two electronic transitions connected by a common intermediate level, is an effective technique for populating high energy electronic levels in an atom. Such excitation can be very useful for laser enhanced ionization (LEI) spectrometry, since sensitivity is often limited by the ability to populate an excited state which is close enough to the ionization limit to be efficiently ionized. The feasibility of stepwise LEI was demonstrated in 1979 [1] using a dual N_2 laser-pumped dye laser, but relatively poor limits of detection were achieved. An improved stepwise LEI system has been assembled for the present work, based on dye lasers pumped by a Nd:YAG laser.

Detection limits for stepwise LEI using the present system are given in Table 2, along with the single photon detection limits achieved with the Nd:YAG based system and with the flashlamp pumped dye laser system. The detection limit is defined as the concentration which gives a signal amplitude three times that of the blank noise level. In each case studied, the stepwise LEI detection limits are major improvements over previous LEI results and are comparable to or better than those which can be achieved by other methods of analysis. For the first time, sensitive LEI detection of elements with ionization potentials >9 eV is possible. A complete listing of the best values of all LEI detection limits measured to date is given in the periodic table, figure 6. Comparison of the stepwise excitation results (Table 2) to those measured using single photon Nd:YAG excitation shows the signal enhancement obtained by using the second excitation step. In addition to improved sensitivity, the added dimension of a second excitation wavelength improves the selectivity of the method.

Table 2. LEI Detection Limits (ng/mL).

Element	Stepwise Excitation	Single Photon Nd:YAG	Single Photon Flashlamp
Au	1	1000	---
Cd	0.1	100	---
Co	0.08	10	40
Cu	0.07	3	100
Ni	0.08	2	8
Pb	0.09	3	0.6
Sn	0.3	8	2

LEI PERIODIC TABLE

1 H 13.6																1 H 13.6	2 He 24.6
3 Li 5.4 670.8 0.001	4 Be 9.3											5 B 8.3	6 C 11.3	7 N 14.5	8 O 13.6	9 F 17.4	10 Ne 21.6
11 Na 5.1 285.3 0.05	12 Mg 7.6 285.2 0.1											13 Al 6.0 308.2 1	14 Si 8.1	15 P 10.5	16 S 10.4	17 Cl 13.0	18 Ar 15.8
19 K 4.3 294.3 1	20 Ca 6.1 300.7 0.1	21 Sc 6.5	22 Ti 6.8	23 V 6.7	24 Cr 6.8 298.6 2	25 Mn 7.4 279.5 0.3	26 Fe 7.9 302.1 2	27 Co 7.9 252.1 591.7 0.08	28 Ni 7.6 300.3 576.8 0.08	29 Cu 7.7 324.8 453.1 0.07	30 Zn 9.4	31 Ga 6.0 287.4 0.07	32 Ge 7.9	33 As 9.8	34 Se 9.7	35 Br 11.8	36 Kr 14.0
37 Rb 4.2 572.4 1	38 Sr 5.7 460.3 4	39 Y 6.4	40 Zr 6.8	41 Nb 6.9	42 Mo 7.1	43 Tc 7.3	44 Ru 7.4	45 Rh 7.5	46 Pd 8.3	47 Ag 7.6 328.1 1	48 Cd 9.0 228.8 466.2 0.1	49 In 5.8 303.9 0.006	50 Sn 7.3 284.0 597.0 0.3	51 Sb 8.6	52 Te 9.0	53 I 10.4	54 Xe 12.1
55 Cs 3.9	56 Ba 5.2 307.2 0.2	57 La 5.6	72 Hf 7.0	73 Ta 7.9	74 W 8.0	75 Re 7.9	76 Os 8.7	77 Ir 9.1	78 Pt 9.0	79 Au 9.2 242.8 479.3 1	80 Hg 10.4	81 Tl 6.1 291.8 0.09	82 Pb 7.4 283.3 600.2 0.09	83 Bi 7.3 306.8 2	84 Po 8.4	85 At 9.5	86 Rn 10.7
87 Fr 4.0	88 Ra 5.3	89 Ac 6.9	104														
				58 Ce 5.6	59 Pr 5.5	60 Nd 5.5	61 Pm	62 Sm 5.6	63 Eu 5.7	64 Gd 6.2	65 Tb 6.0	66 Dy 6.8	67 Ho	68 Er 6.1	69 Tm 5.8	70 Yb 6.2	71 Lu
				90 Th 7.0	91 Pa	92 U 6.1	93 Np	94 Pu 5.1	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

Figure 6. The best values of LEI detection limits measured to date, including both single-photon and stepwise excitation results. Data given for each element as follows: upper left hand corner — atomic number; upper right hand corner — ionization potential in eV; mid-center — excitation wavelength(s) in nm (2 wavelengths given when stepwise excitation is used); lower-center — the limit of detection in ng/mL.

Several Standard Reference Materials were used to study the performance of stepwise excitation LEI in "real sample" analyses. All samples were dissolved (1 g/100 mL) by wet-ashing using NBS purified acids. The results, given in Table 3, show agreement between the stepwise LEI results and the certified values. The determination of tin in SRM 396 (Copper Benchmark III) is a difficult measurement. Figure 7 shows the LEI signal measured for this sample while scanning the second excitation wavelength over the Sn line at 597.0 nm with the first step LEI transition fixed at the 284.0 nm Sn line. The concentration of the Sn in the dissolved sample was 6.7 ng/mL. The determination is made possible by the low detection limit for Sn and the absence of any significant spectral background interferences.

Table 3. LEI Analysis of Standard Reference Materials.

	LEI Result[a]	Certified Value[b]
SRM 396 (Unalloyed Copper)		
Ni	4.3 ± 0.2 μg/g	4.2 ± 0.1 μg/g
Sn	0.67 ± 0.05 μg/g	0.8 ± 0.3 μg/g
SRM 362 (Low Alloy Steel)		
Sn	0.0156 ± 0.0008 Wt. %	0.016 ± 0.001 Wt. %
SRM 363 (Low Alloy Steel)		
Pb	0.0022 ± 0.0001 Wt. %	0.0022 ± 0.0001 Wt. %
Sn	0.107 ± 0.001 Wt. %	0.104 ± 0.005 Wt. %

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[a] The imprecision quoted is ± one standard deviation, as determined from 10 replicates (not including sample weighing and solution preparation).

[b] Uncertainty as stated on the certificate of analysis.

Continued study and development of the technique is planned in a number of areas. In many cases, the sensitivity which is now possible exceeds that for which the present burner system, developed for atomic absorption, was intended, and many of the detection limits reported in Table 2 are limited by contamination and memory effects. An improved atom reservoir is needed. There remain a number of fundamental areas which require study in order to improve further the limits of detection and selectivity of LEI. Those which we hope to study in the near future are the signal collection mechanism for pulsed lasers, and the spectral background signals which have been observed, but are not fully understood. In addition, much will be learned by continued SRM analysis using LEI.

Reference

[1] Turk, G. C.; Mallard, W. G.; Schenck, P. K.; Smyth, K. C. Anal. Chem. 51: 2408-2410; 1979.

G. C. Turk

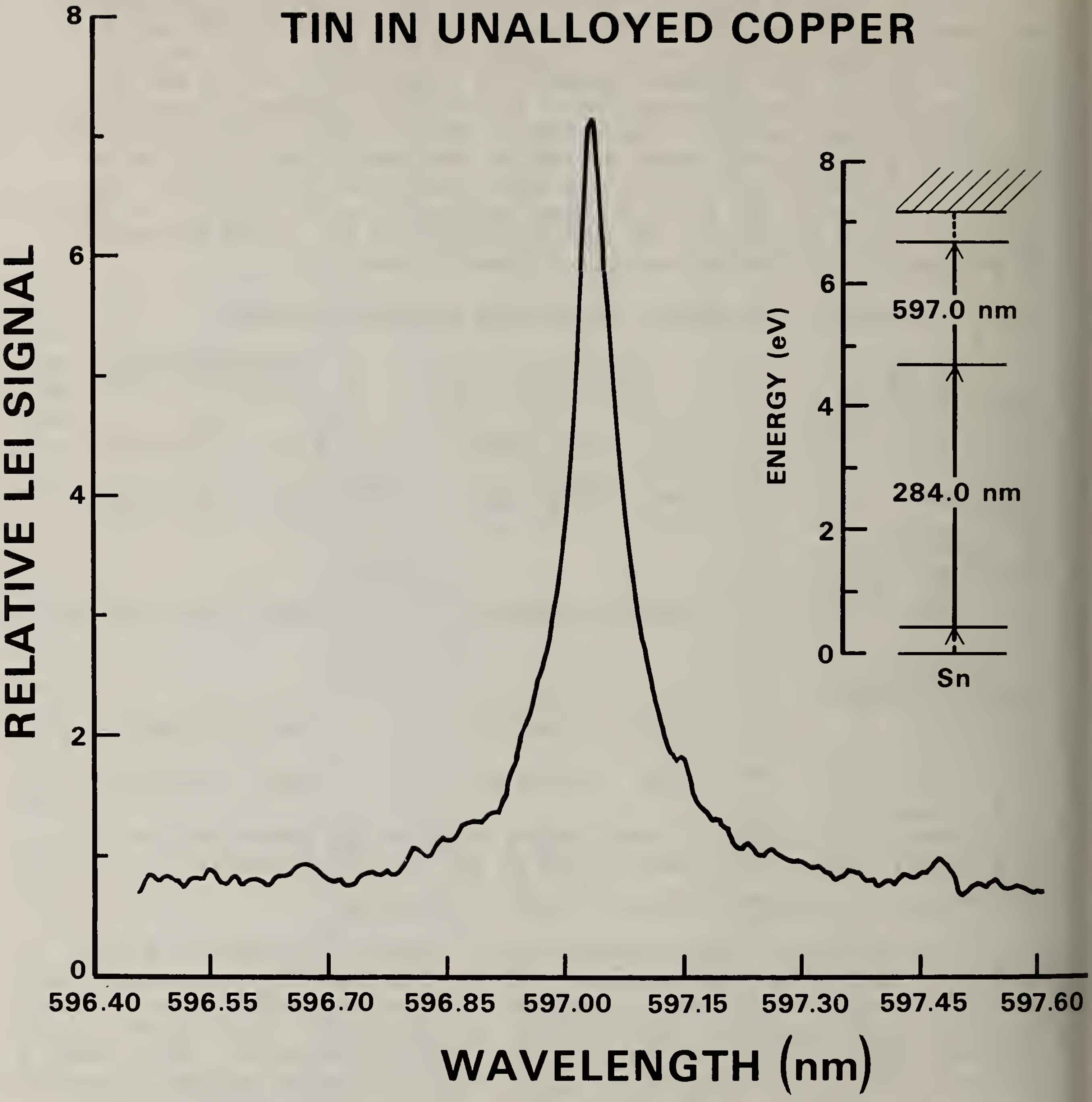

Figure 7. Second step Sn transition at 597.028 nm in unalloyed copper SRM 396 with first step wavelength fixed at 283.999 nm. Sn concentration in solution is 6.7 ng/mL.

d. Spatially- and Temporally-Resolved Studies of Laser-Perturbed Atom Populations in an Analytical Flame

During the course of the studies previously reported concerning the collection of ions in flames [1], it was noted that the efficiency of the CW laser enhanced ionization (LEI) process is sufficiently high to significantly (>50%) deplete the original free Na atom concentration in the laser-irradiated volume of the H_2/air flame. Because of the relative slowness of the diffusion and recombination processes by which this atom-depleted "hole" should return to equilibrium with the surrounding environment, measurable atom depletion persists for several cm above the position of the perturbing laser beam, e.g., ("down-stream" in the ∿10 m/s flame gas flow).

The optical system shown in figure 8 was devised in collaboration with Dr. P. K. Schenck (Chemical Stability and Corrosion Division) to study the spatial and temporal evolution of the "hole" formed by Na atom depletion. A beam splitter (BS) is used to generate a small (<10%) portion of the irradiating laser beam for use as a "probe" beam in spatially resolved absorption experiments. The probe beam is optically isolated with a quarter wave plate (QWP), monitored for laser intensity with a photodiode (PD), and directed by mirrors (M) through a lens (L) and refractor plates (S_V, S_H) into the flame (B). The refractor plates are rotated under stepper motor control to shift the beam horizontally (S_H) and vertically (S_V), providing a ∿4mm x 4mm raster for spatially resolved absorption. After passing through the flame, a portion of the probe beam is directed onto a photomultiplier (PM) through a lens and optical filter (F). The perturbing, or "pump" beam may be modulated or pulsed with an acousto-optic modulator (AOM)/aperture (A) combination before being focused into the flame.

As the pump beam is turned on and off by the AOM (at ∿1 kHz), the transmission of the probe beam is modulated by the periodic atom depletion via an optical absorption process. Lock-in detection of the PM signal coupled with rastering of the probe beam is thus used to generate a contour plot such as shown in figure 9. The contours are linearly spaced at 1 percent increments in transmitted beam intensity. Contours for >10 percent are omitted because of their density near the pump beam position. The flame-like appearance of figure 9 results from the equilibrium production of ions at (0.0, 0.0), the steady upward flow of the flame gases, the diffusion of atoms, and the recombination of electrons and ions.

A less complex picture is obtained by pulsing the pump laser for 20 μs--a time comparable to the transit time of an atom across the beam--and plotting the contour map at 5 μs intervals after the laser pulse. This is done by averaging the PM signal in a 5 μs/channel signal averager at each raster point. A 12-frame subset of the 40-frame "movie" thus obtained is shown in figure 10. The displacement of the hole with time is a ready measure of the burnt gas velocity [2]. Diffusion coefficients and recombination times are currently being extracted by fitting the holes to theoretical functions.

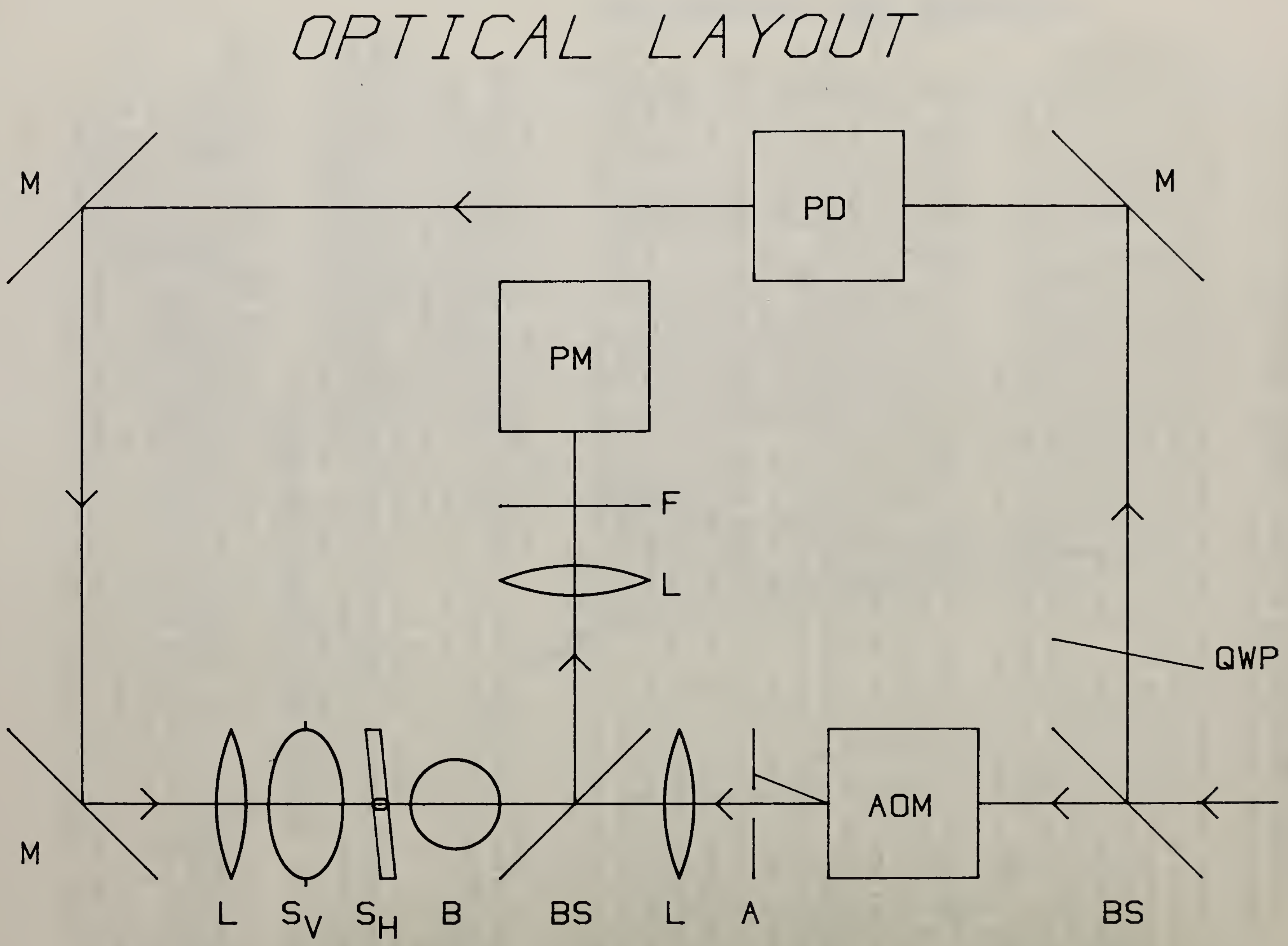

Figure 8. Optical schematic of raster-scan probe of laser atom depletion. See text for symbol definitions.

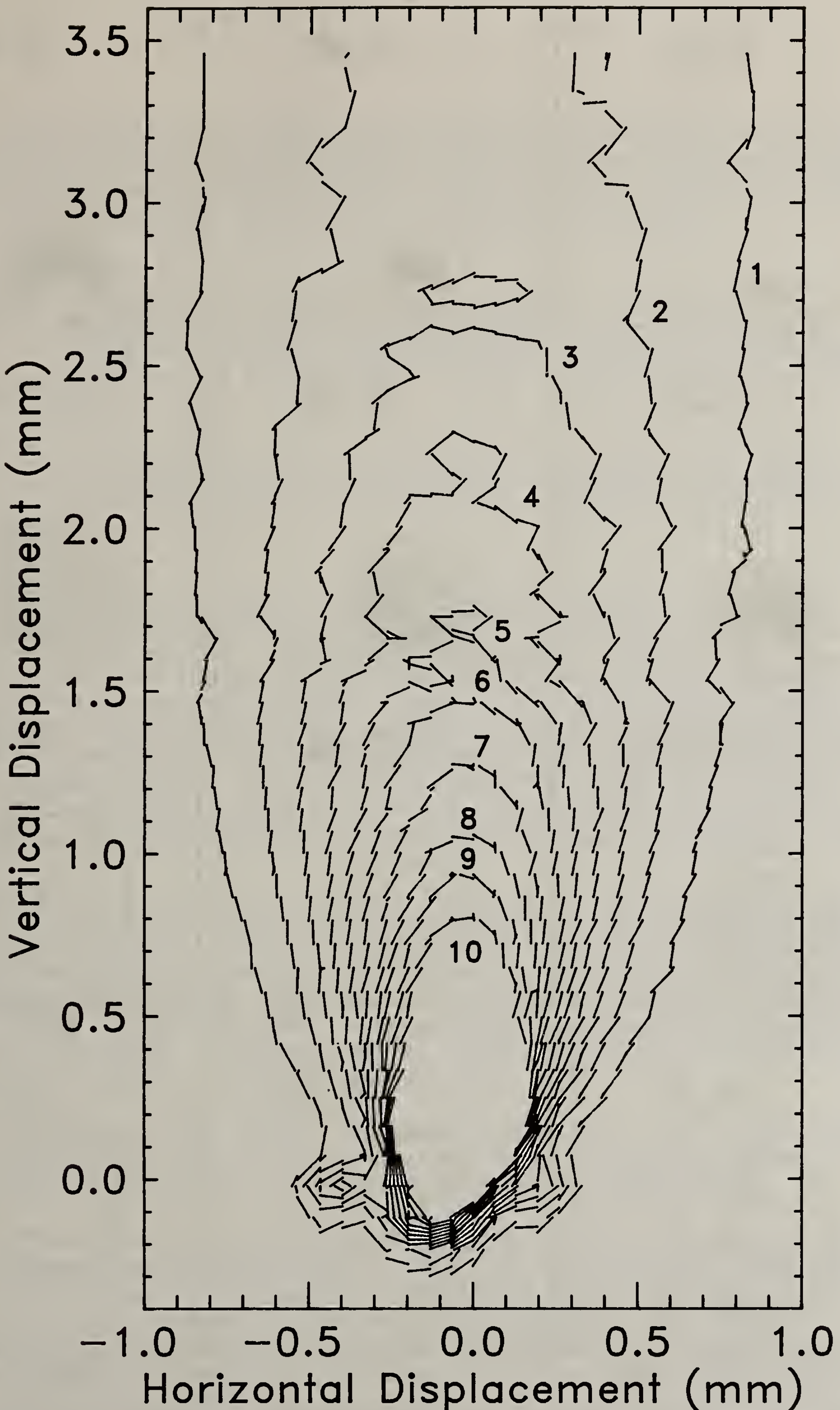

Figure 9. Contour plot of steady state Na atom depletion resulting from continuous laser ionization. Scales are relative to the pump beam position which is 9.5 mm above the burner head. Contours are 1% increments in transmitted light intensity, with an upper limit of 10% to avoid contour bunching. Blank spot in the region $0. \le y \le 0.6$, $-0.2 \le x \le +0.2$ mm is an artifact of the 10% upper limit.

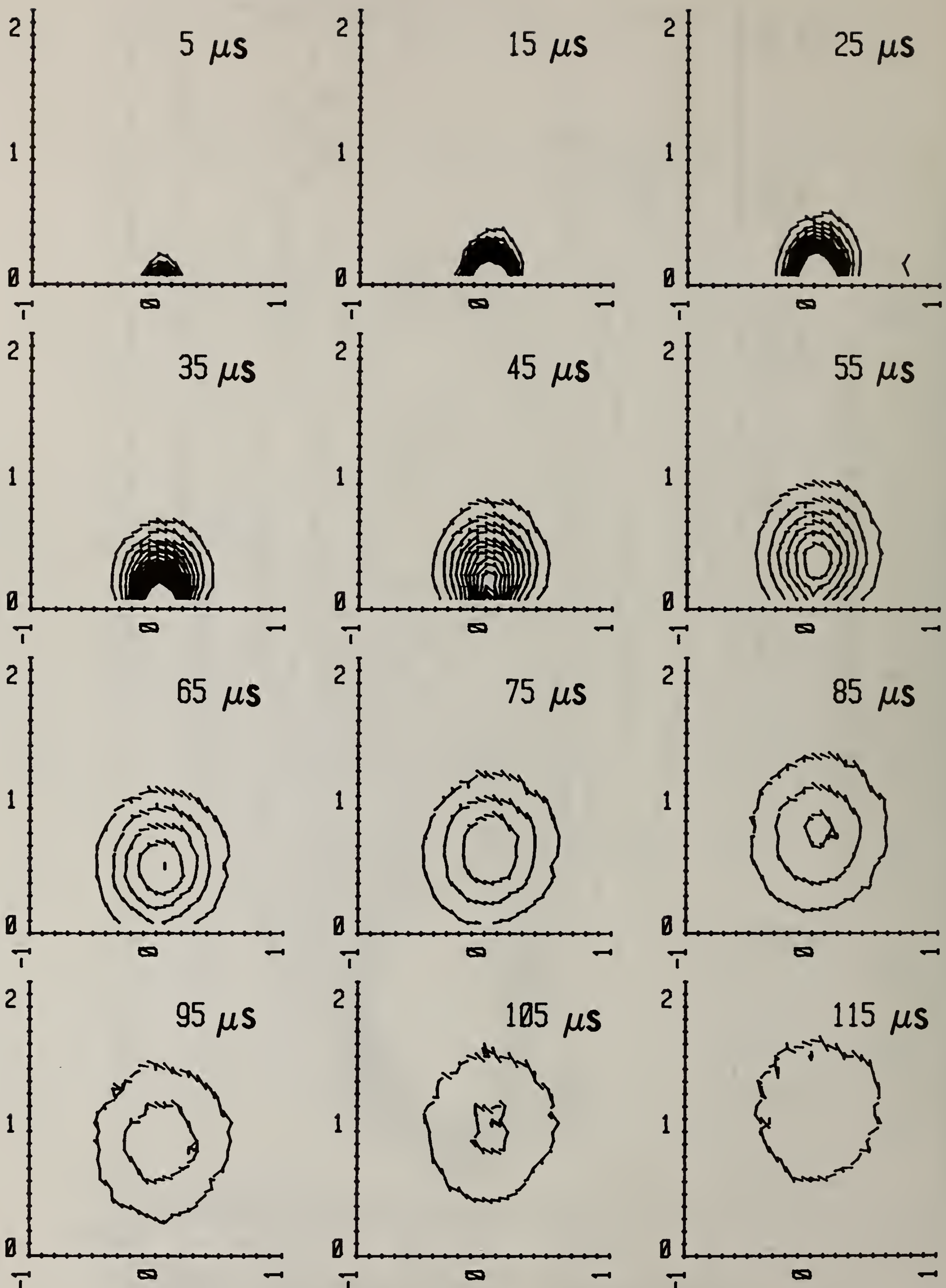

Figure 10. Time-resolved non-linear contour plots of Na atom depletion at 10 µs intervals measured from the beginning of the 20 µs laser pulse. Contours are 1% increments in transmitted light intensity up to a maximum of 15%. Blank region in the center of the 15-35 µs frames is an artifact of the 15% upper limit. 5 µs frame marks pump laser position and tick marks represent 0.2 mm increments in both vertical and horizontal axes.

The raster-probe technique with time resolved detection could be used to study transient atomic excesses as well as depletions. We hope to conduct such a study using UV laser pulses to photo-dissociate refractory oxides in the flame and map the history of the resultant metal atoms.

References

[1] Schenck, P. K.; Travis, J. C.; Turk, G. C.; O'Haver, T. C. "Collection of Ions Produced by Continuous Wave Laser-Enhanced Ionization in a Hydrogen/Air Flame", J. Phys. Chem. 85: 2547; 1981.

[2] Schenck, P. K.; Travis, J. C.; Turk, G. C.; O'Haver, T. C. "Laser Enhanced Ionization Flame Velocimeter", in internal review.

J. C. Travis, G. C. Turk

e. The Use of Microcomputers in the Center for Analytical Chemistry

More than two years have passed since components of microcomputers have been stocked in the NBS storeroom. Once each month a committee made up of knowledgeable users reviews the components that are available and recommends renewal or replacement with totally new or updated ones. The selection of the S-100 bus which is now the IEEE standard 696, along with software based upon the CP/M operating system proved to be a good one, because literally hundreds of hardware components and software packages are available for this system.

There are over 100 microcomputers at NBS that have been assembled from storeroom components. The following systems have been installed in the Center for Analytical Chemistry (Division in parenthesis): a) High Accuracy Spectrophotometer (551); b) Automatic Gas Handling (3) (553); c) Laser (LEI) (2) (550); d) Laser (IR) (550) (see section F-1,a above); e) Low Background Counting (2) (553); f) Electrochemistry (552); g) Software Development (3) (550), and h) Emission Spectrograph (551).

The following are systems now under development: a) Gas Chromatography-Mass Spectrometer (552); b) High Accuracy Spectroradiometer (552); c) Laser Wavelength Meter (550), and d) Carbon-14 Detecting System (553).

A major advantage to this approach is the ability to upgrade the computer by purchasing new components that simply plug into the power-supplied main chassis. For example, our early microcomputers used Intel 8080 microprocessor chips with a clock rate of 2 Mhz with 16-48K bytes of RAM memory and 5 1/4 inch single-density floppy disk drives. The costs for a system began at $1500 and as capability increased, the cost increased to about $3000. The microcomputers which are presently in use contain a Zilog Z80A microprocessor with 4 Mhz clock, 64K bytes of RAM, double density floppy disks and a variety of other peripherals which include: a) A-D and D-A converters; b) Real time and time of year clocks; c) Telephone modems; d) Hardware floating point processors; e) IEEE 488 interfaces; f) CRT terminals; g) Printers; h) Parallel and serial I/O controllers; i) Interrupt controllers, and j) CRT and plotter graphics.

The software available for these microcomputers includes the following: a) CP/M disk operating system; b) Basic interpreter and compiler; c) FORTRAN; d) PASCAL; e) Macroassembler; f) CALCOMP-like graphics library for FORTRAN; g) Word processor, and h) Hardware floating point FORTRAN and BASIC library.

The current average cost of such a system including software is $6000. Interfacing is no more difficult than that required for any type of computer. For example, we installed on the NBS microcomputer an experiment running on a PDP 11-03 microprocessor in 3 days including all software changes from the FORTRAN.

The next step is the entrance into the 16 bit microprocessor era which is now just beginning. Microprocessors with sufficient hardware components and good software to consider stocking in the storeroom are ready for evaluation by the committee at the present time but lack of funds for this purpose is impeding progress. These new microprocessors can directly address one to eight megabytes of main memory. They will have clock speeds of up to 10 Mhz and powerful instruction sets. The high level languages written for this system are to be highly compatible between microprocessors. Some of the 16 bit microprocessors and their approximate computing power compared to an 8080 are shown below. These numbers are approximately the inverse of running time derived from five benchmarks published in EDN magazine: a) Intel 8080 (8 bit) 1; b) Zilog Z80A (8 bit) 2.2; c) Zilog Z800 (8 bit) 5; d) Intel 8088 (8 bit) 7; e) Intel 8086 10; f) Zilog Z8000 13; g) Digital Equipment LSI 11-23 18.6; h) Motorola 68000 21.

Peripherals include all of those for the eight bit microprocessors plus Winchester disks and math coprocessors. A significant new component for the 8088 and 8086 is the mathematics coprocessor which processes math functions using parallel processors. Computation bound jobs can be completed in about a factor ten less time than without the coprocessor. All of the software that exists for the 8 bit systems will be available including some of the popular 16 bit minicomputer operating systems, such as UNIX. The average cost of these systems including 256 K bytes of RAM and a Winchester hard disk (8 M bytes) is about $10,000. Utilization of these microcomputers for equipment control opens new possibilities for the type of computer-experiment interaction that should help to improve the accuracy of analytical techniques.

F. C. Ruegg

f. Inorganic Ion-Doped Glass Beads as Potential Microspectrofluorimetric Standards

Expanding use of fluorescence in immunochemical and cytological analyses as well as particulate analysis has made development of microluminescence standards of increasing importance. The microspheres could be used to: (1) calibrate instruments for stability in intensity measurements and wavelength accuracy; (2) as the basis for interlaboratory comparisons of data; and (3) as relative standards (on absolute standards with absolute calibrations) in the measurement or luminescence intensities. The main spectral regions of interest to microscopists for measurement standardization are in the green (500-575 nm, cellular fluorescing tags using fluorescein isothiocyanate-FITC) and red (600-650 nm, tags using tetramethylrhodamine isothiocyanate-TRITC). The basic purpose of this research was to develop a series of stable, microspheres that fluoresce in the green and red spectral regions.

Inorganic ions in glass matrices were chosen as prime candidates for these reference materials based on previous work [1]. These ion-doped glasses, unlike organic fluorophors, demonstrated excellent stability to photon irradiation. Several experimental glass melts containing different pairs of inorganic fluorophors were produced to determine their spectral emission characteristics. Among the fluorophors used with narrow band spectra were samarium, terbium, europium, and dysprosium ions as well as uranyl and copper ions with broad band spectra. Based on spectral analysis of the preliminary melts, glasses doped with europium and terbium ions were chosen for in-depth studies. Silicate glasses doped with varying concentrations of these fluorophors, were formed into beads 5-100 µm in diameter by flowing sieved, crushed glass particles in air through an oven at ∿1000 °C with subsequent cooling and sphere collection on filters. A microscope equipped with an incident-light excitation system and a scanning monochromator for determining emission spectra was used as the basic microspectrofluorimetric system. A high pressure mercury lamp with appropriate filters was used as the excitation source. Excitation radiation impinged on the luminescent bead and the emitted radiation, dispersed by the 0.1 m monochromator, was measured by a photomultiplier tube. The photomultiplier tube output was fed to an amplifier and then directly to a plotter or multichannel analyzer.

Typical emission spectra of the beads doped with terbium, europium, and terbium + europium are given in figure 11. Irradiation for more than 20 hours of the europium + terbium-doped bead gave a constant europium to terbium emission ratio and no indication of fluorophor "fade". Reproducibility studies of the ratios gave standard deviations of approximately 1 percent. The peak maxima of both europium and terbium emissions were proportional to the fluorophor concentration, and at constant fluorophor concentrations, were proportional to the cube of the bead diameter over the range of bead sizes 5-50 µm thereby indicating a homogeneous medium. A very small amount of beads are available for research purposes only and plans to produce these SRM's are underway.

Reference

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J. R. DeVoe, D. K. Hancock, R. A. Velapoldi, D. H. Blackburn, (Center for Materials Science)

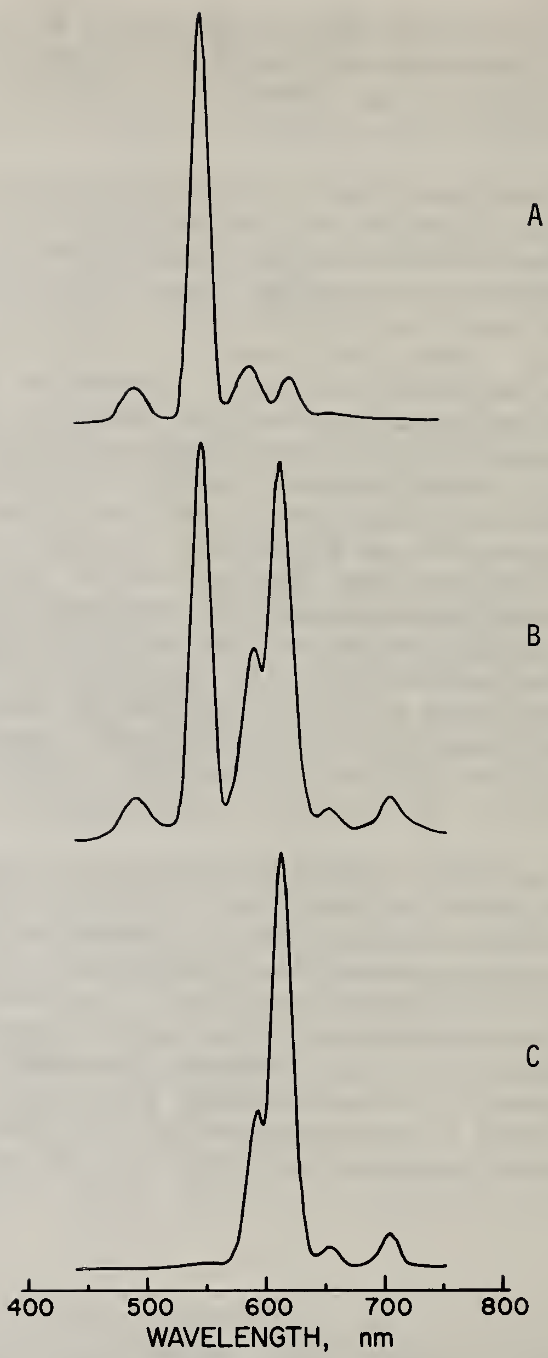

Figure 11. Typical luminescence spectra of inorganic ion-doped microspheres: A-Tb only; B-Tb+Eu; C-Eu only.

3. Outputs and Interactions

a. Publications

Havrilla, G. J. and Green, R. B., "Evaluation of Plate Electrodes for Laser-Enhanced Ionization Spectrometry", *Anal. Chem.*, *52*, 2376-2383 (1980).

Sams, R. L. and Olson, W. B., "Analysis of the High-Resolution Infrared Spectrum of the ν_2 Bending Mode of HOCl at 1238 cm^{-1}", *J. Mol. Spec.*, *84*, 113-123 (1980).

Turk, G. C., "Reduction of Matrix Ionization Interference in Laser-Enhanced Ionization Spectrometry", *Anal. Chem.*, *53*, 1187-1190 (1981).

Travis, J. C. and DeVoe, J. R., "The Optogalvanic Effect", *Lasers in Chemical Analysis*, Chapter 5, Hieftje, G. M., Travis, J. C., and Lytle, F. E., eds., The Humana Press, NJ, 93 (1981)

Scheeline, A., Norris, J. A., Travis, J. C., DeVoe, J. R., and Walters, J. P., "Particulates Formed by a Stabilized High Voltage Spark Discharge", *Spectrochem. Acta*, *36B*, 373 (1981)

Scheeline, A., Travis, J. C., DeVoe, J. R., and Watters, J. P., "Discovery of an Electrical Post-Pulse in the Surroundings of a High Voltage Spark Discharge", *Spectrochem. Acta*, *36B*, 153 (1981).

Havrilla, G. J. and Green, R. B., "Electrode Positioner for Laser-Enhanced Ionization Spectrometry", *Anal. Chem.*, *53*, 134-135 (1981).

Havrilla, G. J. and Green, R. B., "Pre-Amplifier for Laser-Enhanced Ionization Spectrometry", *Chem. Biomed. Environ. Instrum.*, *4*, 11 (1981).

Schenck, P. K., Travis, J. C., Turk, G. C., and O'Haver, T. C., "Collection of Ions Produced by Continuous Wave Laser-Enhanced Ionization in a Hydrogen/Air Flame", *J. Phys. Chem.*, *85*, 2547-2557 (1981).

Sweger, D. M. and Sams, R. L., "Diode Laser Spectra of the ν_2 Band of $H_2{}^{12}CO$ and $H_2{}^{13}CO$", *J. Mol. Spec.*, *87*, 18-28 (1981).

Maki, A. G. and Sams, R. L., "High Temperature, High Resolution Infrared Spectral Measurements on the HNC-HCN Equilibrium System", *J. Chem. Phys.* (accepted for publication 1981).

Maki, A. G. and Sams, R. L., "High Resolution Infrared Spectrum and Structure Determination for Carbon Diselenide (CSe_2)", *J. Mol. Spec.* (accepted for publication 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.* (accepted for publication 1981).

b. Talks

Travis, J. C., "Laser Enhanced Ionization in Flames for Trace Metal Analysis", Chemistry Department Seminar, University of Florida, Gainesville, FL, October 22, 1980. Invited

Travis, J. C., "Trace Metal Analysis by Laser Enhanced Ionization", Chemistry Department Seminar, University of Maryland, College Park, MD, October 31, 1980. Invited

Travis, J. C., "Metres, Meters, and Bovine Liver: A Biased View of the National Bureau of Standards", Austin College Alumni Lecture Program, Sherman, TX, November 20, 1980. Invited

Ehrlich, D. J., Osgood, R. M., Deutch, T. F., Turk, G. C., and Travis, J. C., International Conference on Lasers 1980, New Orleans, LA, December 15, 1980. Plenary Lecture

Travis, J. C., "Laser-Excited Ionization Spectroscopy", Short Course, Department of Chemistry, University of Arkansas, Fayetteville, AR, January 26-28, 1981. Invited

Travis, J. C., "Ion Production and Collection Following Laser Excitation of Atoms in Flames", Department of Chemistry Seminar, University of Arkansas, Fayetteville, AR, January 26, 1981. Invited

Travis, J. C., "Ion Production and Collection Following Laser Excitation of Atoms in Flames", University of Arkansas at Little Rock, Little Rock, AR, January 29, 1981. Invited

Travis, J. C., Turk, G. C., Schenck, P. K. and O'Haver, T. C., "Neutral Atom Depletion by cw Laser Enhanced Ionization", The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 10, 1981.

Travis, J. C., Turk, G. C., and Schenck, P. K., "Time Evolution of the Depleted Atom Density 'Hole' Following Laser Enhanced Ionization in Flames", VIII Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 24, 1981.

Turk, G. C. and Travis, J. C., "Stepwise Excitation Laser Enhanced Ionization Spectrometry", VIII Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 24, 1981.

Havrilla, G. J. and Schenck, P. K., "LEI Detection of Potassium and Rubidium by Infrared cw Dye Laser Excitation", VIII Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 24, 1981.

Travis, J. C., Discussion Leader for Presentation by Mary J. Wirth on "Spectroscopic Measurements of Molecular Dynamics using Picosecond Lasers", Gordon Research Conference, New Hampton, N. H., Aug. 10, 1981.

Moore, L. J.; Travis, J. C., "Laser Induced Ion Fluorescence in Magnetic Sector Mass Spectrometry", VIII Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, Sept. 22, 1981.

c. Committee Assignments

James R. DeVoe
- CAC Committee on Computer Requirement
- NBS Committee on Selection of Microprocessor for the Storeroom
- NBS Ad Hoc Committee on Equipment

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

II. Inorganic Analytical Research Division

Ernest L. Garner, Chief
Thomas J. Murphy, Deputy Chief

A. Division Overview

The diverse analytical methodology in the Inorganic Analytical Research Division is organized functionally into the four broad areas of 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 for the various research activities at NBS, other Federal agencies and other institutions, either private or public, when requested and appropriate. Within this framework, 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 which is of maximum public benefit, and (3) addressing the need for accurate chemical characterization of inorganic species to make a substantial contribution to the problems of national importance confronting government and industry.

During the past year, the ratio of research to analytical support activities has increased significantly and now reflects a more favorable climate for initiating new areas of research. This improvement is primarily attributable to an infusion of competence research funds for compositional mapping via neutron depth profiling and for studies of ion structures/mechanisms. As a result, significant first-year progress has been made in designing and constructing a facility for neutron depth profiling. When completed, this new research tool will add to our knowledge of particle or compositional distribution in materials of critical importance to the nuclear and solid-state electronics industries. In parallel with neutron depth profiling, new opportunities and approaches to improve the quality of mass spectrometric measurements are being explored by using lasers to develop a better understanding of vaporization and ionization processes in thermal and spark-source mass spectrometry. In conjunction with this effort, other agency proposals offer the opportunity to investigate, in collaboration with the Instrument Development Group, laser-induced fluorescence as a new approach to providing ultra-high sensitivity and selectivity for detection and measurement of isotopes. Additional benefits include the use of laser ionization and laser-induced fluorescence as new diagnostic tools for ionization and ion optics studies.

With competence research as the focal point for exploring new directions in analytical chemistry, the major thrust in the remainder of the Division's research program is directed toward targets-of-opportunity to maintain and improve chemical metrology. During the past year, these broad areas included specimen bank research, industrial related SRM research, methods research for trace elements in hazardous waste, speciation, iodine standards for biological materials, high precision/high accuracy methods development and atomic weight. Within this array of activities, significant progress has been made to extend the sensitivity and selectivity of trace and ultra-trace element determinations. For example, a radiochemical, neutron activation, analytical procedure for the determination of ultra-trace levels of platinum and tin in biological matrices was developed and applied to tissue samples. Another example is the improved method for measurement of sulfur by isotope dilution mass spectrometry which is 10-fold more sensitive than the previous method of choice. Similar distinct breakthroughs in methods research were made for the elements iodine, vanadium, nickel, copper, lead, thallium, cadmium, sulfur, uranium and plutonium in various matrices.

Analytical support of major NBS programs and of programs of other agencies reflects a close linkage with problems of national importance in the areas of Standard Reference Materials, environmental measurements, hazardous waste, recycled oil, nuclear waste, and nuclear safeguards. The intensity of analytical effort required in each of these areas has been gradually reduced and has lead to a better balance between analytical services and methods research. This gradual improvement has been a significant and contributing factor in raising the Division's research posture. Perhaps one of the more significant highlights illustrating the analytical support provided for other agencies has been the production and characterization of a set of quality assurance standards for hazardous waste measurements, an area for which very little standardization exists. With the addition of a sludge quality assurance material, to be completed this year, this set of standards will consist of a coal feedstock, fly ash, bottom ash, and two synthetic leachate standards for use as quality assurance materials on a national scale. The general availability of these materials to both government and industry is expected to provide the basis for overall improvement in determining the concentration of priority pollutant elements in waste materials. Of all the national problem areas currently addressed by the Division, hazardous waste is the only one which seems destined for real growth. All others, including Standard Reference Materials, will probably remain at a constant level of effort or reflect a significant decrease.

Major instrumentation development in the utilization of existing equipment is directed at improving the capability for automation and high accuracy multi-element measurements. Research and development outputs within atomic and molecular spectroscopy have been particularly noteworthy. At present, the inductively coupled plasma (ICP) system can simultaneously determine up to 10 elements. With the interfacing of the ICP to the NBS computer, there has been a substantial enhancement in the ability to correct for interferences and background, and to take advantage of curve fitting and inter-element corrections. These basic developments, along with projected improvements, are expected to yield an increased capability for accurate multi-element determination. In parallel with these developments, major advances are being made with the direct current plasma (DCP) system. One of the more significant advances in DCP has been a better understanding of the possible sources of errors and the modification of the instrumentation for the determination of either 10 or 20 elements in a multi-element mode. Another development has been the acquisition of a new computer and some upgrading of existing detection equipment in the Activation Analysis Group. The Mass Spectrometry Group has made substantial improvements in many of the sub-assemblies which will lead to a fully automated instrument.

For the immediate future, the combination of competence research and better balance of analytical support and research within the NBS program structure will form the foundation for continued improvement in the Division's research climate. This foundation will be expanded with new proposals for competence, Director's reserve, and STRS funds. Where practical, the creative and innovative ideas of the staff will be directed at other government agency programs in a manner which will augment the existing research base provided by the various sources at NBS. In addition, the Division will pursue, in collaboration with the Center, those areas of analytical chemistry which have been identified in the Long-Range Plan as appropriate for increased growth or new direction.

1. Activation Analysis Group: Overview

Basic and applied research in activation analysis continues to be focused on procedures leading to better sensitivity, higher selectivity, and increased accuracy. The major goal is to fulfill the needs of analytical chemistry for simultaneous determination of many constituents in complex matrices over a broad dynamic range. The utilization of activation analysis as a versatile and sensitive tool in all branches of science and technology and the development of novel applications are further objectives. Building on the fundamental principles of activation analysis which have remained unchanged, the Group's research efforts resulted in incremental and crucial improvements of the technique. Emphasis is given to procedures, which can leave the sample intact for other uses after analysis, as well as destructive procedures, which enhance sensitivity and selectivity following the analytical irradiation step. A high level of competence has been developed for various activation analysis techniques which include instrumental and radiochemical neutron activation analysis (INAA and RNAA), photon activation analysis (PAA), prompt gamma activation analysis (PGAA), and nuclear track technique (NTT). Concurrently, the Group is expanding its research activities to include questions of general analytical importance such as sampling and sample preparation for analysis.

Recent research accomplishments in the area of activation analysis methodology are highlighted by the development of RNAA procedures for the determination of platinum and tin in biological matrices. In both cases, radiochemistry lowers the limit of detection and provides essentially "background-free" counting of the specific signals, free of interferences from chemical blanks. Unprecedented low levels of platinum have been determined using this new RNAA technique. Other research efforts are directed towards the determination of light elements as major constituents of complex matrices using PAA and PGAA. The accuracy and precision are currently being evaluated. A newly developed RNAA technique for the ultra-trace determination of I-129 will make possible the issuance of a certified material.

In connection with the pilot National Environmenal Specimen Bank (NESB) program, research efforts have resulted in a better understanding of the sampling characteristics of particulate biological matter. Methods to better homogenize these materials have been investigated and developed. Investigators, in collaboration with NBS statisticians, are examining the question of proper subsampling in order to produce more meaningful analytical results. Among the problems being studied are the appropriate number of samples to be taken as well as the proper sample size to be used for analysis.

INAA multielement determinations have provided a huge data-base for Chesapeake Bay, NESB, and Hazardous Waste, the major environmental programs participated in during the past year. The wide dynamic range of activation analysis, along with its multielement capability, is especially useful for the determination of various concentrations of expected elements as well as the detection of unexpected elements. INAA multielement results have been reported for the certification of up to 20 elements in each of a variety of new or renewal SRMs: Bovine Liver, Orchard Leaves, Cast Iron Alloys, Basalt, Obsidian, Reduced Iron Ore, and Fuel Oil. INAA has provided vital information to another NBS Group on fused silica glass insulators. INAA has also been used for the determination of halogens as well as other constituents in organic liquids in support of the NBS Recycled Oil Program and the Office of Standard Reference Materials.

Continued emphasis is placed on the importance of acquiring and utilizing state-of-the-art equipment to assure that INAA, the Group's strongest competence, will continue to contribute to the mission of analytical chemistry at NBS in the same way in the future. Major additions to counting equipment and the acquisition of a computer will help achieve this goal. In addition, the Group will continue to take advantage of the specifics of nuclear techniques in ultra-trace determinations and chemical speciation studies by developing RNAA techniques and applying activation analysis to problems such as the rapidly expanding field of bio-technology. The new depth-profiling facility provides entry into a new and important field in analytical chemistry.

Rolf L. Zeisler, Group Leader; David M. Allen, M. James Blackman, B. Stephen Carpenter, Kathleen A. Fitzpatrick, Ronald F. Fleming, Robert R. Greenberg, Sally H. Harrison, John K. Langland, Richard M. Lindstrom, George J. Lutz, Trudi E. Mitlehner, Michael D. Vinocur, James R. Vogt

2. Analytical Mass Spectrometry Group: Overview

The primary objectives of the Analytical Mass Spectrometry Group continue to be the development and maintenance of a capability for high accuracy isotopic ratio measurements. The increasing need for such high quality analytical measurements on sub-microgram amounts of material has required continual improvement in chemical separation and purification techniques and mass spectrometric instrumentation. To accomplish these tasks, 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 group's work. Expertise in separations technology, isotope equilibration, sample dissolution, purification, and "contamination-free" sample handling are primary concerns in this area. The other 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 had a very favorable research to analytical support ratio, due primarily to the additional research funds received through the Competence Building Program for the investigation of ionization mechanisms and ion structures. Extensive research plans have been formulated for this activity, a laboratory has been modified, and special purpose equipment either has been ordered, purchased, designed, or constructed. A Neodymium-Yttrium Aluminum Garnet (Nd:YAG) laser is scheduled for installation late this year and will be used for ion fluorescence measurements to study vaporization and ionization mechanisms.

Considerable progress has been made on modifications of instrumentation and on the development of fully automated, high-accuracy mass spectrometers. A prototype automatic magnetic field controller has been constructed and successfully tested. A new prototype filament control unit was built, tested, and found to improve stability by two orders of magnitude. A "new" collector without transmission grids has been designed and evaluated. A new electrometric amplifier has been designed and a prototype constructed. These advances will improve existing instrumentation as well as provide the foundation for fully automated high accuracy instruments in the near future. In addition, because of the potential safety hazard from mercury, most of the mercury diffusion pumps have been replaced with turbomolecular pumps.

In atomic weight research, two of the more recently redetermined atomic weights, strontium and silver, have been accepted as international values by the Commission on Atomic Weights of IUPAC. The silver atomic weight impacted on the recently NBS-determined value of the Faraday, reducing the uncertainty in that value by one-half. Research programs to obtain new atomic weights for gallium and lithium are underway.

Important accomplishments in the area of improved methodology for isotope dilution mass spectrometry include the development of chemical and mass spectrographic procedures for elements not previously measured or at lower levels than previously determined. For example, a new thermal ionization silica gel method for sulfur has been developed which offers a 10-fold improvement in precision and accuracy over the spark source method. A method for the determination of picogram quantities of uranium in environmental samples was developed. The first IDMS determination of vanadium was successfully accomplished for the Trace Elements in Oil SRM. Silica-gel procedures were developed which make possible the determination of nickel and copper at much lower concentrations than have been accomplished in the past. A method was developed for the determination of low concentrations of both Pb and Tl on small samples of liver. An IDMS method for Cd in Blood at the nanogram level was developed and applied to "round-robin" samples obtained from the World Health Organization.

The most sample intensive program was measurements on the IDA-80 samples, a joint effort with the Central Bureau for Nuclear Measurements (Belgium) to characterize samples which will be used in a worldwide interlaboratory test program to assess the state-of-the-art of uranium and plutonium measurements by IDMS. In other related research for the nuclear community, high sensitivity pulse counting mass spectrometry was utilized to determine the isotopic composition of nanogram quantities of uranium and plutonium for "round robins" designed to evaluate the state-of-the-art for resin bead technology. These "round robins" involved the distribution of uranium-loaded beads, plutonium-loaded beads, and beads containing both uranium and plutonium. The results indicate measurement precisions comparable to what is achieved with large samples and conventional detectors.

The expertise of the Group was utilized for several programs not involving mass spectrometry. A high accuracy titrimetric method for uranium has been developed in which the sample size requirement has been reduced from 2 g to less than 100 mg with no loss in precision. A program was initiated to evaluate the parameters influencing the accuracy and precision of leachability tests on storage materials proposed for nuclear waste disposal. In addition, reference samples were prepared and/or evaluated for both drilling mud and synthetic "synfuel discharge." Both of these materials will be utilized on a national scale by other government agencies as quality assurance standards.

During the past year, the activities of the Group have been augmented by several long term guest workers. These include scientists from the National Institute of Metrology, Beijung, Peoples of Republic of China; the Central Bureau of Nuclear Measurements, Geel, Belgium; the Institute of Physics, University of Mexico; and the Smithsonian Institute, Washington, DC. Gas isotope dilution mass spectrometry, the origin of artifacts by lead isotopic composition, theoretical studies of isotopic fractionation, and research in isotope dilution to determine Pb and Cd in blood, serum, and other biological fluids are representative of the more significant activities of guest workers.

Near-future research plans are focused on the competence research for ion mechanisms, the atomic weight program, and the development of chemical and mass spectrometric procedures for isotope dilution analyses. The use of a laser as an alternative ionization mode for spark source mass spectrometry remains high on the Group's priority list. Another signficant project is the investigation of simultaneous dual collection of ion currents as an alternate means of increasing precision and accuracy. In parallel with competence and related research activities, Group plans will focus on more automation of ion exchange chromatographic procedures and mass spectrometric analysis. New chemical separation techniques and mass spectrometric methodology to lower detection limits for all elements presently determined will be given major attention. As part of the continuing effort to upgrade existing methodology, research to develop methods to detect and analyze elements currently beyond the Group's capability will be pursued.

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, Billy R. Hardas, Emerson F. Heald, Mark S. Hutzler, William R. Kelly, Howard M. Kingston, George M. Lambert, Lawrence A. Machlan, Eddy A. I. Michiels, John R. Moody, Larry J. Moore, Pedro A. Morales, Paul J. Paulsen, Lura J. Powell, Ronald W. Shideler

3. Atomic and Molecular Spectrometry Group: Overview

The Atomic and Molecular Spectrometry Group strives to advance the development and analytical applications of emission and absorption processes occurring in the spectral region of 2000 to 8000 Å for the improved characterization of a wide variety of materials in an efficient and cost-effective manner. The areas currently being addressed to achieve this goal include the development of: (1) more accurate methodologies; (2) expanded multi-element capabilities; and (3) state-of-the-art calibration standards.

The Group's research efforts in atomic spectrometry have centered primarily on the continued development and evaluation of the analytical capabilities of the inductively coupled plasma (ICP) and the direct current plasma (DCP)/echelle spectrometers. Up to 10 elements can presently be determined simultaneously with the ICP system; 10 and 20 element dedicated cassettes have been installed and aligned for use in the DCP instrument.

In order to characterize and correct for matrix effects, the ICP minicomputer has been connected to the NBS computer via the NBS network. This data transfer capability should significantly improve the accuracy of ICP analyses. In addition, laser machining is presently being investigated as a possible technique for precisely machining slit arrays with slit widths of 20 micrometers or less. To date, in-house capabilities have been successful in producing arrays containing a maximum of only three slits with minimum widths of about 70 micrometers.

Two principal factors have been identified that seriously affect the accuracy of measurements with the DCP instrument. One is related to the types of spectral interferences encountered; the other is related to the significant wavelength shift produced in the echelle spectrometer by small changes in room temperature. Both single and multielement studies of spectral interference are under study and various ways for thermostating the spectrometer are being considered.

Two important research projects were initiated in atomic absorption (AA) with potentially large long-term payoffs. One is concerned with the search for a universal matrix modifier to eliminate interferences in graphite furnace measurements and the other involves an initial evaluation of a coupled high performance liquid chromatograph-AA detector for performing metal speciation measurements. Both of these projects, over the next several years, are expected to eventually lead to improved accuracy and sensitivity for trace element analysis.

Spark emission spectrometry is presently used extensively to provide acceptance, homogeneity, and elemental data for metal SRM's. In providing these services during the past year, two areas were identified that merited further study. In the first one, work was carried out to understand and correct for the general problem of sample contamination during analytical preparation; in the other area, work was done to evaluate an apparent bias in spark emission sulfur values for certain iron-base SRM's.

Two major research efforts have been carried out in molecular spectrometry this year. The first effort involved the identification and elimination of the polarization problem that has hindered the production of the chromium-on-quartz transmittance standard (SRM 2031). By more carefully controlling the rate of evaporation of the chromium and spinning the quartz plate during deposition, the polarization effect, which in severe instances was larger than 10 percent, has been reduced to less than 1 percent. The second effort involved the development of a prototype luminescent uranium glass standard for use in calibrating instrumentation employed in the evaluation of fluorescent dye penetrants used in non-destructive crack testing.

Again this year, the large effort in analytical support activities by the Group represents a very substantial contribution to programs of national importance. Programs to which the Group made major contributions were Standard Reference Materials, Recycled Materials, Hazardous Waste, Nuclear Waste, Environmental Specimen Bank, FDA Injectables, and Service Analyses. A few of the programmatic accomplishments made during the past year include: The collection, processing, and characterization of a fly ash, a sludge, and two levels of a 17-element simulated solid waste leachate for use by DOE and EPA as quality assurance standards; the multielement graphite furnace-AAS analysis of 36 liver specimens, and approximately 60 injectable materials; and initial characterization of leachates obtained from various glasses being evaluated as underground storage containers for nuclear wastes.

Future plans entail expanding the current but modest efforts in metal speciation studies, initiating research for the direct analysis of solids by graphite furnace-AAS, developing a capability for measuring the particle size distribution in spark-generated aerosols, adapting the DCP instrumentation for vacuum UV applications, and continuing the systematic investigation of matrix modification techniques.

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

4. Electroanalytical Chemistry Group: Overview

The Electroanalytical Chemistry Group has as its objective the development and utilization of electrochemical principles for chemical analysis. The techniques of interest include amperometry, conductimetry, coulometry, ion chromatography, polarography, and potentiometry. Research is aimed at attaining a more thorough understanding of the complex chemical systems encountered during the development and implementation of high-accuracy procedures ranging from ultra-trace determinations in a myriad of matrices to assays of ultra-pure chemicals. Electrochemistry is experiencing a resurgence in popularity and this Group intends to take an active role through innovative research incorporating all of these techniques, particularly in the areas of speciation and multi-component analysis.

One of the major responsibilities of this Group is in support of the Standard Reference Material program, both in research and in analysis for certification. This year, basic research was undertaken to extend the capabilities of ion chromatography to the determination of sulfur in steel and in copper alloys, and preliminary results appear promising. It is expected that this method development will be completed next year and that its application to real samples can begin. High-precision coulometry was used to certify three primary standard chemicals, tris (hydroxymethyl)aminomethane, benzoic acid, and potassium dichromate. Extensive measurements were made on the dichromate samples during an exhaustive statistical study to establish homogeneity. At the same time, systematic uncertainties in coulometry were also studied. Aluminum was determined in several samples of cast irons by polarography. River Sediment, Urban Particulate, and Washington Dust were analyzed by ion chromatography for total sulfur, chlorine, and soluble sulfate and chloride. Several oils were analyzed for sulfur content using ion chromatography.

The major effort of polarographic analysis this year focused on the analysis of human liver samples for trace metals as part of the National Environmental Specimen Bank. In addition, another project was initiated to analyze biological and injectable materials for trace metals, particularly aluminum. These analyses are part of a program to establish the trace metal composition of the different types of injectables currently in use. After establishing normal trace levels for the various product types, a suitable matrix will be selected and a reference material will be characterized to serve as a control or standard for the determination of trace metals in biologics.

The Acid Rain program is continuing with an increased emphasis on research. The goal in this area is the development of an SRM which will provide traceability to the national measurement system through a few well characterized standards rather than a large number of audit samples. Long-term stability of acid rain reference materials in various containers is being investigated. Serious shortcomings have been found in the methods for pH and acidity measurements as well as in subsequent interpretation of the data. For instance, residual liquid-junction potentials can severely bias the pH measurement. Acidity titrations can be similarly affected by errant end-point selection or end-point detection by inappropriate techniques. Revised measurement protocols are being investigated to correct these deficiencies.

A small synfuel waste discharge project was completed which involved a critique of the sampling and measurement procedures recommended by EPA, and the preparation and analysis of two sets of solutions containing select elements and anions for use as control standards. Standards used to calibrate the ion chromatograph were put on an absolute basis through the use of coulometric standardization of high-purity acids. Methods were developed for the complete anionic characterization of chloride-doped cadmium sulfide by ion chromatography. Additionally, the distilled water in the Chemistry Building is checked regularly by this Group using conductimetry and ion chromatography to ensure its quality.

Significant advances have been made in the high-precision coulometric assay of uranium. A comprehensive study of current efficiency was made involving different electrode materials and surfaces in a variety of electrolytes. This study has resulted in a procedure with twice the precision of earlier high-precision methods.

This past year, the major instrumentation acquired was an electrochemical detector to complement the conductimetric detector of the ion chromatograph. It is expected that it will be used in the coming year for cyanide determinations and halogen speciation.

A major effort will be initiated next year toward upgrading the pH facility and reestablishing the expertise for recertification of NBS pH buffers. Paralleling this effort will be research in pH measurements of low ionic strength solutions such as encountered in acid rain samples. Commencing with these two projects, it is hoped to generate vigorous research activity in pH and potentiometry. Research in high-precision coulometry will continue with studies of current efficiency and other systematic errors which may adversely affect the accuracy of the method. Voltammetric research will tend toward the utilization of anodic stripping voltammetry for precise trace and ultra-trace metal analyses. Investigations in ion chromatography will concentrate on incorporating the electrochemical detector into the system to enhance selectivity and sensitivity and to augment the types of anions determinable. Methods for determining speciation of halogens, nitrogen, sulfur, and possible metal anionic complexes will be explored. A joint project coupling the selective pre-concentration of trace metals by electrodeposition with the sensitivity and specificity of atomic absorption is anticipated.

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B. Selected Technical Accomplishments
(Inorganic Analytical Research Division)

1. Application of Sampling Theory to Particulate Biological Samples

The quality of the analytical sample, as distinguished from the quality of the chemical measurement, is a too often disregarded factor in analytical chemistry. The sample on which the results of a chemical analysis are finally based depends very much on the properties of the bulk sample and the analytical test portion taken from the bulk sample. Programs like the pilot National Environmental Specimen Bank (NESB) are critically dependent on the credibility of the analytical results, e.g., on the bulk sample representation found in the analytical test portion. The NESB tasks of evaluating storage conditions and analytical quality are carried out by means of multiple analysis of many samples. This represents an ideal test case for studying the application of sampling theory to the investigation of the properties of particulate biological materials.

Biological specimens, (e.g., human liver, mussel, etc.) are homogenized at cryogenic temperatures under contamination-free conditions, in Teflon ball and disk mills to provide analytical test portions for comparative analysis. The samples are always handled in a cryogenic state and maintain particulate appearance after homogenization. Assuming a particulate homogenate, the performance of the two types of mills, ball and disk, was investigated. A radiotracer experiment was carried out and Ingamells sampling constant, K_s, was determined after collecting the data for a sampling program [1]. Using the ball mill, a $K_s = 32$ g was determined. Based on the K_s value, one can conclude whether the material has been adequately ground and adequately mixed. As a result of this study a disk mill was designed that yielded a K_s of 0.95 g.

To verify the particulate model, efforts were undertaken to actually measure the particle size distribution of the homogenate obtained from the two different milling procedures.

In general, sieving experiments are an easy way to determine particle sizes; however, cryogenic sieving of frozen samples is much more difficult. After some procedure development, the sieving experiments were carried out in a large LN_2 freezer which provided the necessary cold and dry atmosphere to avoid melting and particle agglomeration due to moisture condensation. The results of sieving split liver samples, previously ground in the two different mills, show that the disk mill produces somewhat finer particles with virtual elimination of the coarse (>40 mesh) fraction. Twenty five percent of the material ground in the ball mill remained in the coarse (>40 mesh) fraction. The obvious affect on subsampling is that smaller particles produce better homogeneity.

Using the information about particle size distribution and some assumptions as to the chemical nature of the liver, the weight of sample required to hold the sampling standard deviation to a preselected level can be theoretically calculated starting with the computation of N, the number of particles.

The value of N may be calculated from the relation

$$N = \left[\frac{d_1 d_2}{\overline{d}^{\,2}}\right]^2 \left[\frac{100(p_1 - p_2)}{R\,\overline{p}}\right]^2 p(1 - p)$$

where d_1 and d_2 are the densities of the two kinds of particles, $\overline{d}$ is the density of the sample, P_1 and P_2 are the percentage compositions of the component of interest in the two kinds of particles, $\overline{P}$ is the overall average composition in percent of the component of interest in the sample, R is the percent relative standard deviation (sampling error) of the sampling operation, and p and 1-p are the fractions of the two kinds of particles in the bulk material [2]. For a two component particle mix made up of cells and fluids and for 40 mesh particles, the element Na requires a one gram sample to reduce the sampling error to one percent. This is very consistent with the sampling constant of 0.95 g found as described above.

In addition, trace element analysis experiments were carried out to provide support data for the theoretical evaluations. In one experiment, ten subsamples of homogenized liver were analyzed using nuclear methods for about 30 elements. The element specific homogeneity was determined to be two to three percent for most elements and one percent or less for Na, Fe, and Zn. In another experiment, mussel (Mytilus edulis) samples were homogenized in a disk mill before being sieved. The sieved fractions were then analyzed by Instrumental Neutron Activation Analysis (INAA) for trace elements. Representative percentages of the amount of material in each sieve fraction are also given. Some interesting results from this experiment are shown in Table 4. These results indicate a fraction containing NaCl, probably due to the salt water contained in the mussel shell at the time of shucking, which being ice crystals, grinds to a finer particle size than the organism material.

Table 4. Na and Cl in Mussel Sieve Fractions.

(concentration in mg/g dry weight)

Sieve Fraction Mesh Range	<40	40-60	60-80	80-100	100-140	140-200	<200	Unsieved
Weight Percent	2	25	18	14	26	12	3	
Na	54.0	53.8	57.2	61.9	65.5	70.7	71.8	61.0
Cl	79.8	96.7	102	110	116	121	128	111

The work shows that theoretical calculations of sampling parameters compare favorably with experimental results. This information can provide important knowledge on the relation of the analytical test portion to bulk material and therefore the quality and usefulness of the analysis.

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2. Determination of Ultratrace Platinum in Biological Materials

Increasing interest in the determination of platinum has been spurred recently by the widespread use of the element in industrial and medical applications. Two possible major sources contributing to the human body burden are the noble metal catalysts used to reduce automobile emissions, and the administration of platinum-containing drugs used in cancer chemotherapy. The intense interaction of platinum and its complexes with biological systems makes it desirable to establish baseline data and to monitor possible increases in human body burden. Previous attempts to measure baseline concentrations of platinum have failed because the reported sensitivities were several ng/g for the various techniques, while the actual concentrations were at least one order of magnitude lower. Many analytical techniques including neutron activation, however, have been successfully applied to monitor elevated platinum levels, e.g., after administration of anticancer drugs consisting of platinum complexes of the cis-($PtCl_2L_2$) type [1].

To measure the naturally occurring concentrations in human tissues and other biological materials, a new neutron activation analysis scheme based upon radiochemical separation of the activation products has been developed. This method fully utilizes the inherent sensitivity of the activation reaction $^{198}Pt\ (n,\gamma)\ ^{199}Pt$ and counting of the daughter nuclide ^{199}Au after radiochemical separation. The separation applied here is highly specific for gold, thus avoiding common interferences as well as providing "background free" counting of the respective gamma activities. A decontamination factor of $>10^7$ for ^{24}Na has been achieved. The only remaining interference to be considered is the reaction $^{197}Au\ (n,\gamma)\ ^{198}Au\ (n,\gamma)\ ^{199}Au$ from the naturally occurring gold in the samples. This reaction can be quantitatively assessed with high precision and taken into account by the determination of the gold using the same separation step. This analytical procedure, therefore, also provides excellent results for gold at the 10^{-12} g/g level.

The results of a number of applications of the method to biological Standard Reference Materials and human liver specimens are given in Table 5. The results for platinum are found to be far below previously reported data for Orchard Leaves, SRM 1571, and below the current limit of detection in this material. The gold values, however, are in good agreement with the previous data, thus confirming the completenesss of the analytical scheme [2]. For Bovine Liver, SRM 1577, both elements seem to be inhomogenously distributed, which would explain the wide scatter of the previously reported data for gold. The platinum concentrations found here are the first data reported for a presumably natural baseline in these materials which were collected more than ten years ago. It would be of interest to analyze similar materials collected recently. Possibly an increase of platinum in the environment could be detected.

The application of the technique to the analysis of human liver specimens collected in the National Environmental Specimen Bank Program will help to establish baseline information on human body burden.

Table 5. Platinum and Gold in Biological Materials.
Concentration, 10^{-12} g/g (dry weight)

	This Work		Literature [2]	
	Pt	Au	Pt	Au
SRM 1571, Orchard Leaves	∿200	1430 ± 80[a]	(89.2 to 1200^{6})$\cdot 10^{3}$	1970 to 3500
SRM 1572, Citrus Leaves	60 ± 30[a]	107 ± 9	NR[b]	NR[b]
SRM 1577, Bovine Liver	70 ± 30	56 ± 13	NR[b]	200 to 30000
Human Liver	50 to 240	69 to 2650	NR[b]	30 to 100000

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[a] Experimental error, fewer degrees of freedom.

[b] No data reported previously.

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3. A New Method for the Determination of Sulfur by Thermal Ionization Mass Spectrometry

The determination of sulfur in ferrous and copper materials at concentrations below 50 ppm is necessary to control critical chemical and physical properties of these materials. Classical chemical methods for measuring sulfur are not applicable to concentrations much below 50 ppm and the newer instrumental techniques applicable at these concentrations rely on calibration curves based on standards. To produce Standard Reference Materials for these instrumental determinations, it is necessary to have an independent technique capable of yielding an absolute sulfur determination with microgram sensitivity. A thermal ionization mass spectrometric isotope dilution procedure has been developed to meet these needs.

This procedure utilizes much of the chemistry previously developed for the isotope dilution spark source mass spectrometric (ID/SSMS) determination of sulfur (0.5 µg blanks, and ±3 percent rsd). The reason for adopting isotope dilution thermal ionization mass spectrometry was two-fold, first to lower blank levels (ID/SSMS blanks are limited by sulfur content of the gold powder necessary for sample preparation) and second to utilize the inherently more precise thermal ionization method.

Sample and ^{34}S spike are equilibrated in a sealed pyrex tube to prevent loss of volatile sulfur compounds prior to equilibration. The sulfur is isolated, converted to As_2S_3, dissolved in NH_3 plus excess As(III), and loaded onto a Re filament with silica gel. Sulfur isotopic ratios are measured as the AsS^+ ion. Since As is mono-nuclidic, the ion intensities at masses 107, 108, 109, and 111 from AsS^+ are directly proportional to the abundances of sulfur 32, 33, 34, and 36, respectively.

Currently, the blank is 0.1 µg or less and the measurement precision for the $^{34}S/^{32}S$ ratio is better than 0.2 percent. This represents a five-fold improvement in blank levels and a ten-fold improvement in precision and accuracy compared to ID/SSMS.

Sulfur determinations have been obtained for two copper base SRM's and are given in Table 6. Three aliquots of a 2.7 gram spiked sample of SRM 184 were chemically processed and measured independently. The results are affected by blank from the chemistry and the mass spectrometry as well as the precision of ratio measurements.

Table 6. Parts Per Million Sulfur by Weight.
(µg/g)

	SRM 184	SRM 1035
	17.70	22.30
	17.74	22.15
	17.63	22.19
Average	17.69	22.21 ppm

The blank correction was about one percent in each case. The measured values show a 0.6 percent range which indicates the present level of control over the three sources of error and imprecision mentioned above. Also given in Table 6 are three separate determinations on a composite chip sample of SRM 1035. In this case, the values obtained are affected by the three previously mentioned factors as well as sample heterogeneity. The relative range in SRM 1035 is also about 0.6 percent. These sulfur determinations indicate that precise sulfur determinations can be obtained at the 20 ppm level and that sample heterogeneities of one percent could be resolved at this level on one gram samples.

Blank control is critical in sulfur analysis due to the high sulfur levels inherent in chemical laboratories plus the ambient levels due to internal combustion engines and fossil fuel power plants. Isotope dilution sulfur blanks are now being held below 0.1 µg by excluding room air with a nitrogen gas blanket whenever the samples are not in a sealed system.

The mass spectrometric sample requirements for a single analysis are in the submicrogram range. With this level of sensitivity, the three major isotopes can be measured very precisely. This eliminates a potential bias of one percent due to the natural variation of the sulfur isotopic composition.

The precision with which the $^{32}S/^{34}S$ ratio can be measured by this technique permits the possible identification of distinct sulfur sources. One important application would be the study of the sulfur isotopic ratios in rain as a means of identifying the sulfur source as coming from coal, oil, gas, or soils. This technique, while not yet as precise as "gas" mass spectrometric isotopic ratio measurements, has the advantage of using simpler chemical premeasurement processing and an approximately 10-fold smaller sample.

The high precision of this thermal silica gel procedure makes it suitable for high sulfur levels in addition to the low levels reported so far. With precisions of better than ±0.2 percent rsd, this technique will be competitive with any other method at concentrations up to and above 1000 ppm. The method will be applied shortly to determining sulfur in Citrus Leaves and Bovine Liver SRM's.

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4. An Investigation of Biases in the Determination of Sulfur in Steel by Emission Spectrometry

Over the past several years, the need to accurately determine sulfur in steel has assumed greater importance. This is particularly true where certain physical properties of steel are adversely affected by concentrations of sulfur greater than 0.005 percent. The acute need for reliable quality assurance materials with accurately known trace sulfur concentrations for steel production is reflected in industrially related SRM research to develop definitive methods. With the availability of such data, calibration of other instrumentation utilized to characterize reference materials or provide quality control analyses for the steel production process is the next essential step.

Most of the sulfur values reported by emission spectrometry over the last few years have been based on calibration data obtained from the NBS SRM 1260 series of low alloy steels. Prior to the recent isotope dilution spark source mass spectrometric (ID/SSMS) validation of the sulfur content of these five SRM's, the emission spectrometric calibration curve was established by drawing the best line through five data points.

Considering that isotope dilution mass spectrometric values are in general the most accurate available, it was noted that when emission intensity was plotted as a function of the ID/SSMS value, two distinct curves could be drawn. One curve came from SRM 1265 and SRM 1262 and the other from SRM 1261, SRM 1263, and SRM 1264 (figure 12). The displacement between these two curves corresponds to a discrepancy in sulfur concentration of about 0.002 percent. These curves are best defined using the Walters adjustable waveform excitation source but are also seen with the recent new source from

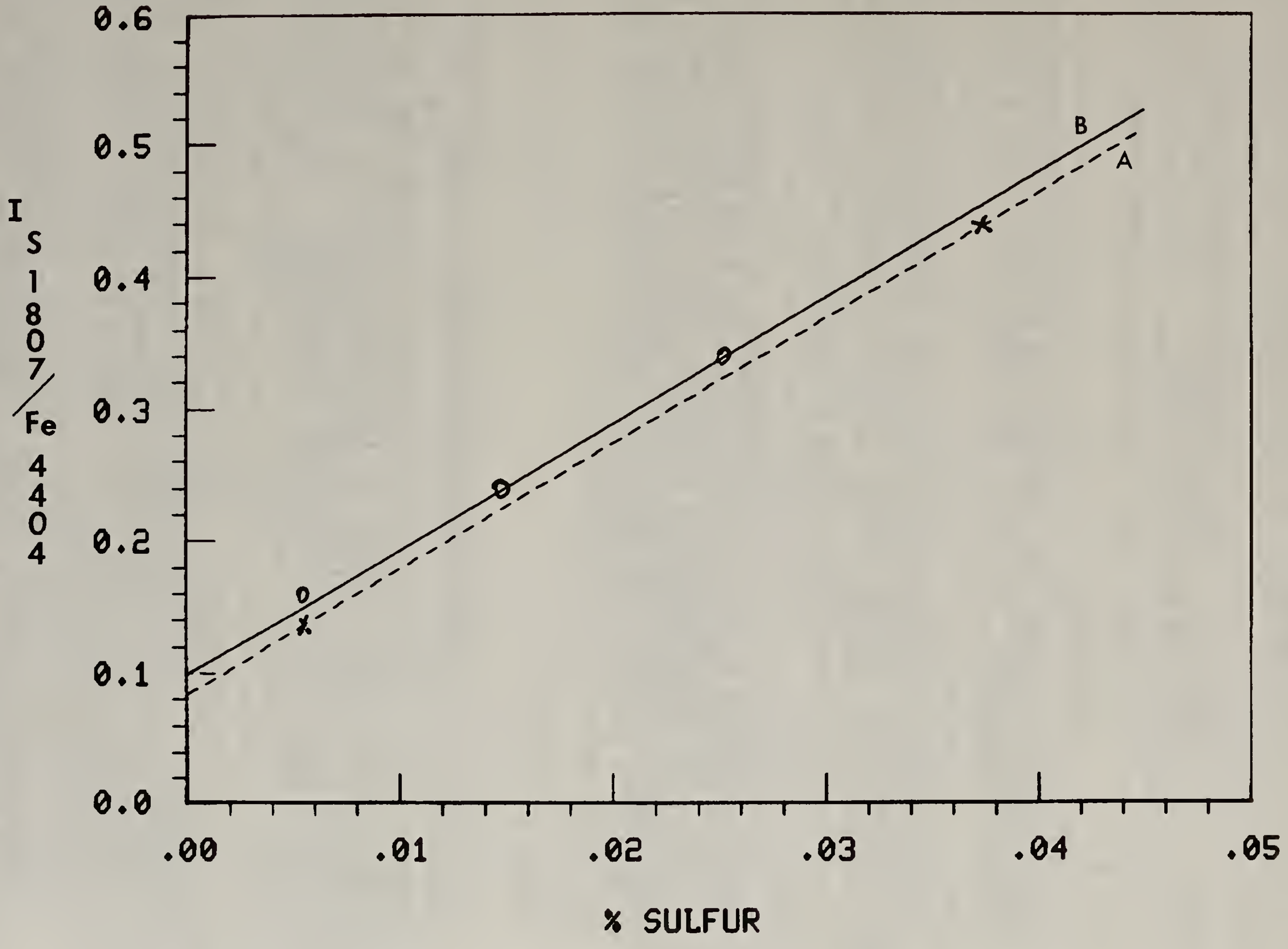

Figure 12. Analytical curves for sulfur in steel — AWS 80:30.

Baird Corporation (KH-3). As new production SRM's have become available, they also divide between the two curves. Other special research materials show the same pattern although most materials fall on the same curve at concentrations below 0.01 percent. The SRM's evaluated thus far are grouped as follows:

Curve A	1265, 1262, 1138A, 1134, 1167, 1165, 1166, 1270, 131b, and high purity iron
Curve B	1263, 1261, 1264, 1138, 1163, 1161, 1222, 1161, and 1269

Values for SRM 1164, SRM 1162, and SRM 1168 do not fall on either curve but are found above curve B. No values have been found for SRM's below curve A.

Reference materials from other sources have also been evaluated. Since the given sulfur values are not related to the present definitive values, the data are scattered between the two curves. New chemical determinations directly related to the new sulfur values are needed to properly place these materials.

The identification of a bias of 0.002 percent in the determination of sulfur in steel by emission spectrometry has profound and far reaching implications in the understanding of excitation chemistry mechanisms. Until additional research is conducted to identify the source of the bias, reliable quality control by emission spectrometry in the production of steels with less than 0.005 percent sulfur will be difficult.

D. E. Brown, J. A. Norris

5. Determination of Chlorine and Sulfur in Cadmium Sulfide

Cadmium sulfide, doped with various elements, has been used extensively in the photoconductor and solar energy industries. Recently, there has been renewed interest in cadmium sulfide doped with cadmium chloride for use as a possible super-conductor at non-cryogenic temperatures. The concentration of chloride and its manner of incorporation (either within the crystal lattice or merely as an intimate mixture) may be critical parameters to the effectiveness of the compound as a super-conductor. Previous methods for the determination of halogens in these types of materials required expensive instrumentation, extensive sample preparation, or were plagued with severe matrix interferences and non-specificity. Procedures have now been developed for the rapid determination of not only chlorine but all the anionic components in cadmium sulfide samples.

To determine total sulfur and chloride content, the samples were dissolved in a 1:1 mixture of a carbonate buffer solution (pH 9.8) and hydrogen peroxide (30 percent), with gentle heating. Under these conditions, all sulfur species were oxidized to sulfate, whereas the chloride was unaffected. After destroying the excess peroxide by boiling, the sulfate and chloride were quantitated using ion chromatography. Total sulfur and chloride were then computed, as well as mass-balance, assuming the sample contained only cadmium sulfide and cadmium chloride.

In order to determine the soluble anionic components, the cadmium sulfide samples were sonicated in an ultrasonic bath using a carbonate buffer solution as the solvent. Identification and quantitation of the anions were performed by ion chromatography. In the materials analyzed, only chloride and sulfate have been found as soluble components. However, had other soluble anionic species (such as fluoride, bromide, nitrate, or phosphate) been present as contaminants, they would also have been determined.

Eighteen samples have been analyzed with total chloride ranging from 0.7 to 4.0 percent by weight and soluble chloride ranging from 0.1 to 2.5 percent by weight. Those samples wherein all the chlorine was present as soluble chloride did not exhibit super-conducting properties. All the samples contained some sulfur as sulfate, but at a concentration always less than 0.4 percent by weight. The estimated precision of these analyses is five percent (one standard deviation). This uncertainty could be reduced to one percent by additional research if future studies require better precision.

In conclusion, a new method has been developed for the analysis of cadmium sulfide samples for anionic constituents. Speciation of the chlorine and sulfur components has been demonstrated. Work is proceeding to extend the method to bromine as well. An alkaline hydrogen peroxide procedure has proved to be effective in the dissolution of cadmium sulfide. It is anticipated that such a dissolution procedure could be applied to other metal sulfides and sulfur-bearing materials, with the subsequent determination of total sulfur as sulfate by ion chromatography.

W. F. Koch, J. W. Stolz

6. Determination of I-129 in Biological Matrices

Iodine-129 is present in the environment in both natural and man-made forms. The major man-produced sources are nuclear weapons tests and irradiated nuclear fuel reprocessing plants. Recent emphasis on increasingly reliable I-129 measurements has prompted modification of existing methods in an effort to improve accuracy and to develop a Standard Reference Material certified for I-129 content.

Neutron activation analysis is used for the measurement of the fission produced I-129 in biological and environmental samples. The determination consists of a pre-irradiation separation, irradiation in the reactor, and a post-irradiation separation. The pre-irradiation separation involves the combustion of the sample in a stream of oxygen; the "off gases" are filtered through glass wool to trap out any particulate material and the iodine is trapped on activated charcoal. This pre-irradiation filtering removes uranium, cesium, and tellurium which interfere with the determination of I-129 by yielding, upon irradiation, the activation product I-130.

The charcoal trap containing the iodine is then sealed in quartz and irradiated in the reactor at a thermal neutron flux of $1.5x10^{13}$ for a period of 16 hours. After a short cooling period, a few milligrams of inactive iodine carrier is added. The charcoal and carrier are burned in a stream of oxygen. The gases evolved are again passed through a plug of glass wool to filter out particulate material. The collecting trap consists of a bed of hydrated manganese dioxide (HMD) followed by a charcoal trap for collecting the iodine. HMD is one of a series of selective ion retention media developed during the past several years. It is usually used for separations from aqueous solutions but has been applied to gas phase separations.

Over a fairly wide temperature range, HMD will remove in excess of 99 percent of chlorine and bromine from the gas stream while passing greater than 90 percent of the iodine. However, decontaminations of approximately 10^8 are required for radiobromine; hence, three or four passes are required.

The preliminary studies have been completed and work is commencing on the measurement of the I-129 content of the SRM's 1648, Urban Particulate Material and SRM 1572, Citrus Leaves. Samples of these SRM's have been distributed to three other laboratories in the United States active in the field of I-129 analysis. It is expected that this round robin can be used to certify the I-129 content of the samples.

G. J. Lutz

7. Analysis of Human Liver for Baseline Lead and Thallium

The National Environmental Specimen Bank is involved in a pilot program to monitor the effect of the increasing influx of anthropogenic sources of trace elements on human health. To accomplish this, it is imperative to collect accurate baseline data regarding the concentration of environmentally important substances in the present population so that future changes can be detected. Lead and thallium are two elements that are known to be toxic at trace levels. To achieve the required levels of sensitivity and accuracy, an isotope dilution mass spectrometric (IDMS) method was developed and applied to tissue samples. Since the available samples were small (0.5 g) and the expected concentrations low (1-5 ppb Tl), blanks for the procedure would have to be extremely low. A method that accomplished these objectives was developed using SRM 1577a, Bovine Liver, as a control sample.

A number of 0.5 g samples of this material were spiked with ^{206}Pb and ^{203}Tl, wet ashed using nitric and perchloric acids, and heated to remove excess acid by evaporation. Lead and thallium were then simultaneously separated by anodic electrodeposition as PbO_2 and Tl_2O_3. The mixed deposits were dissolved from the electrodes and their altered isotope ratios were determined by thermal ionization mass spectrometry. Thallium isotope ratios were measured first, at a low temperature (700 °C), and then lead isotope ratios were measured at a higher filament temperature (1200 °C).

The results of the determinations of Pb on 0.5 g samples of SRM 1577a, Bovine Liver, yielded an average value of 0.136 ± 0.012 µg Pb/g compared to 0.134 ± 0.08 µg Pb/g for one gram samples using a more extensive separation technique (Pb only). The thallium concentration was found to be 3.1 ± 0.1 ng Tl/g. Lead blanks for the procedure averaged 2.0 ng Pb and the thallium blanks averaged 0.03 ng Tl.

Lead and thallium concentrations were then determined in thirteen samples of human liver using the same procedure. The results are shown in Table 7.

Table 7. Concentrations of Lead and Thallium and Their Relative Ratios.

Sample	Concentrations μgPb/g	 ngTl/g	Ratios Pb/Tl
1	4.38	1.70	2576
2	3.21	2.11	1521
3	2.15	1.85	1162
4	2.56	5.31	482
5	1.31	1.24	1056
6	1.11	6.24	177
7	2.83	1.02	2774
8	0.90	1.31	687
9	4.16	1.21	3436
10	0.71	7.07	100
11	3.41	1.32	2583
12	6.05	4.66	1298
13	1.15	2.16	532
SRM 1577, Bovine Liver	0.134	3.1	43
Earth's Crust[a]			20
Granite[a]			33
Shale[a]			20
Basalt[a]			40

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[a] Source - R. D. Reeve and R. R. Brooks, "Trace Element Analysis of Geological Material," J. Wiley & Sons, N. Y., NY, 1979, pp. 80-81.

The results are interesting in that they show that while thallium concentrations in human liver are in the same range as for bovine liver (1-7 ng Tl/g compared to 3 ng Tl/g), lead in human liver is considerably elevated over bovine liver (1-6 μg Pb/g compared to 0.1 μg Pb/g). This increase becomes more evident when one compares the ratio of lead to thallium. For most of the human liver samples, this ratio exceeds 1000/1 while the ratio for bovine liver is near that of the earth's crust and various rocks, 20-40/1. This could be due to the fact that cattle are less exposed to major anthropogenic sources of either lead or thallium. On the other hand, humans are exposed to anthropogenic sources of lead but not of thallium. Thus monitoring the trend of Pb/Tl ratios could be an indicator of the degree of lifetime exposure to anthropogenic lead sources.

J. W. Gramlich, T. J. Murphy

8. Development of a Radiochemical Separation Procedure for Tin

Although tin has been shown to be essential for mammalian nutrition [1], it can be highly toxic in some forms [2]. Unfortunately, tin cannot be readily determined in biological materials because of the naturally occurring low levels. For example, very few biological reference materials with known tin concentrations are available. None of the eight NBS biological SRM's issued have either certified or "information only" values for tin. Relatively little reliable data concerning the tin concentrations in human and animal tissues and fluids exists.

Neutron activation analysis can be used to determine tin in most biological materials at the naturally occurring levels if a radiochemical procedure is used to separate tin from interfering elements and the background level of radiation (noise) is reduced. Both the ^{113}Sn and ^{117m}Sn isotopes can be used to quantify tin if the interfering ^{160}Tb (for ^{113}Sn) and ^{47}Sc (for ^{117m}Sn) isotopes are removed. This has been accomplished with a separation procedure based on the extraction of SnI_4 into toluene. The sample is initially dissolved with nitric, sulfuric, and hydrofluoric acids along with hydrogen peroxide, followed by a filtration step to remove precipitated oxides and sulfates from the final sulfuric acid solution before extraction into toluene. Carriers are used to assure a quantitative recovery (>99.8 percent) and maximize the decontamination.

Five samples of SRM 1571 (Orchard Leaves) have been analyzed by the above procedure. The resulting preliminary value for concentration of 290 ± 17 (1s) ng/g agrees favorably with two of the literature values (294 ± 16, 290 ± 20, and 4100 ng/g) compiled by Gladney [3]. The resulting reduction in background radiation was better than a factor of 1000, and no Sc or Tb could be detected using other, more intense, γ-rays, indicating decontamination factors of >20,000 for Sc and >1000 for Tb.

Research is continuing to further improve this method. A small fraction of the selenium, $\sim$1 percent, accompanies the tin through the separation and can elevate the background around the tin peaks in some matrices. Therefore, efforts will be directed at selenium reduction. Other SRM's with lower tin concentrations, such as Bovine Liver (SRM 1577), will be analyzed to evaluate the suitability of this procedure to provide certification quality data for new SRM's.

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R. R. Greenberg

9. Development of a Fluorescent Glass Standard for Calibration of Instrumentation Used for the Evaluation of Dye Penetrants

Fluorescent dye penetrant testing is used extensively for the nondestructive detection of flaws in a wide variety of test objects. As currently practiced, the procedures lack both reproducibility and reliability both in the dye application and development techniques as well as in the measurement of fluorescence. Undoubtedly, at the present state-of-the-art, many components with damaging flaws are now passed while others are wrongfully rejected.

In order to provide a valid basis for using fluorescent dye penetrant testing as a reliable screening device, work has been undertaken to evaluate uranium-doped glasses as comparative fluorescent standards for use in standardizing instrumentation. Two types of standards are currently in different stages of preparation and evaluation. The first type consists of a single, rectangular piece of Corning 3750 glass mounted in a metal heat sink that provides temperature stability of the glass during prolonged irradiation periods. An engineering drawing of this assembly is shown in figure 13. The main body of the metal block is type 2024 aluminum that has been anodized flat black and the bottom plate is brass. The slot milled in one half of the aluminum holder has been precision machined to provide a close fit with the glass. Final positioning of the fluorescent glass, exactly flush with the top of the holder, is accomplished under a microscope. It is subsequently held in place by filling the 1 mm void between the bottom of the glass and the brass plate with a black adhesive. Ten of these units have been built thus far and are now undergoing extensive homogeneity and accelerated stability testing. Initial measurements, obtained by mapping the surface of these glasses in grid-fashion with a microspectrofluorimeter having a circular measuring aperture of 25 micrometers, indicate that the fluorescence does not vary more than two percent.

In addition to the ten heat sink units, two other units modified for water thermostating have also been fabricated. These will be used to accurately measure the temperature coefficient of the uranyl fluorescence in this particular batch of glass. As soon as the above studies are successfully completed, these assemblies will be sent out to the manufacturers and users of fluorescent dye penetrants for further evaluation and comment.

A second type of standard in the early stages of design and production employs glass fibers having various uranium concentrations and diameters in order to obtain a graded series of fluorescent intensities and widths of indication. Previously prepared fibers having nominal uranium concentrations of 0.6 to 2.5 weight percent and diameters of 5 to 50 micrometers are being considered for this purpose [1].

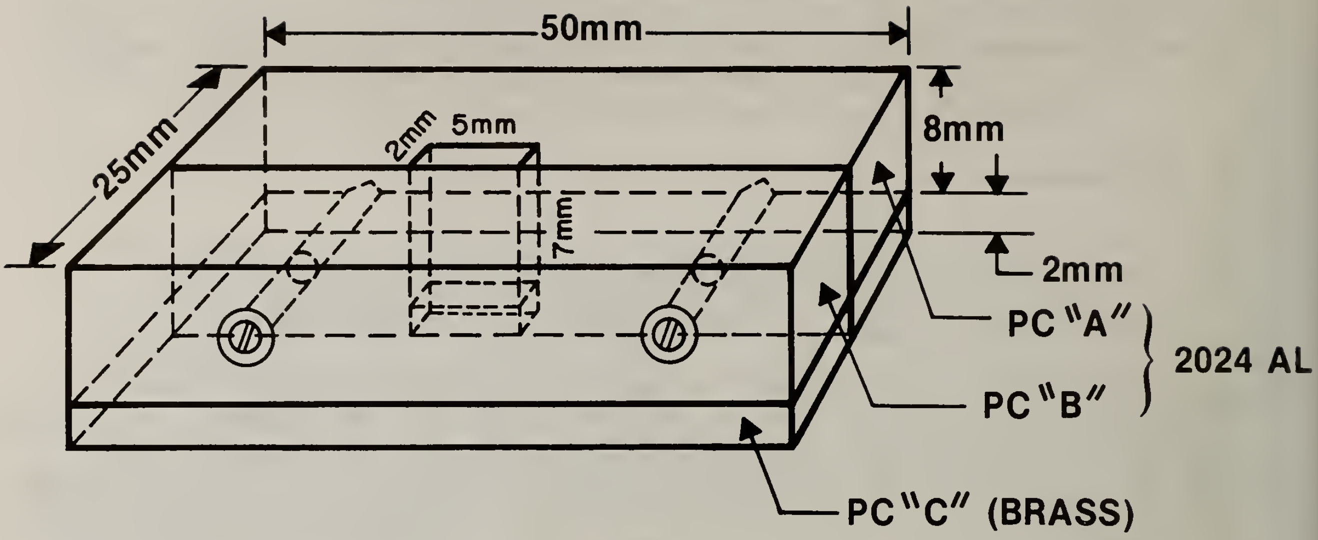

Figure 13. Fluorescent uranium glass and heat sink assembly.

Present plans call for making two variations of these fiber standards. One will have a fixed uranium concentration and various diameters that approximate the widths of the indications commonly obtained in crack evaluation; the other will consist of a series of fibers having the same diameter and various uranium concentrations. Each type will be sandwiched between two nonfluorescent quartz plates with a transparent cement whose refractive index closely approximates the refractive index of the fiber. The diameter and relative fluorescent intensity of each fiber in a series will be specified. The final production, characterization, and testing of these fiber standards will form the main thrust of our effort in FY 82.

Reference

[1] Velapoldi, R. A.; Travis, J. C.; Cassatt, W. A.; Yap, W. T. J. Microsc. 103: 293; 1975.

R. W. Burke, D. K. Hancock, R. A. Velapoldi

10. Determination of Halogens in Organic Liquids by Neutron Activation Analysis

The technological usefulness as well as the environmental hazard of an organic liquid, especially an oil, is often directly related to its halogen content. The partitioning of each halogen-containing component among the various organic fractions of the liquid, in addition to being of scientific interest, may point the direction toward effective purification. For these reasons, an accurate and reliable means of halogen analysis over a broad concentration range is desirable.

Organic liquids provide nearly ideal matrices for neutron activation analysis since carbon, nitrogen, hydrogen, and oxygen produce no countable radioactivity. Each of the halogens, on the other hand, produces an activation product with its own unique half-life and gamma-ray energy, as shown in Table 8.

Table 8. Neutron Activation Products for the Halogens.

Element	(N,γ) Product	Half-life	Gamma-ray Energies, keV
Fluorine	^{20}F	11.0 sec	1633.8
Chlorine	^{38}Cl	37.2 min	1642.2, 2167.6
Bromine	^{82}Br	35.3 hr	554.3, 776.5, 1044.1 ...
Iodine	^{128}I	25.0 min	442.9

The short half-life of ^{20}F dictates accurate timing ability and for that reason fluorine analysis has not been exploited routinely. On the other hand, since the fluorine activity will decay away rapidly, its presence at any level does not degrade the measurement of the other halogens. Conversely, because it has the longest half-life, large amounts of bromine will reduce the sensitivity for the other halogens, yet bromine can be measured in the presence of any amount of them. In effect, the different half-lives provide an automatic and complete "chemical separation" of fluorine, bromine, and the other two halogens. Of course, since modern gamma-ray spectrometry systems have energy resolution of better than 2 keV (FWHM), the lines used for quantification are well resolved.

Significant progress has been made during the past year on the measurement of halogen concentrations in organic liquids. Among the several developments are: (1) The reliable, accurate, simultaneous determination of chlorine and bromine has been demonstrated in a variety of lubricating oils as part of the ASTM/NBS basestock consistency study under the Recycled Oil Program [1]; (2) The determination of total chlorine homogeneity in oils doped with polychlorinated biphenyls (PCB) has been carried out in the development of the PCB SRM-1581; (3) In collaboration with the Tribochemistry Group of the Center for Materials Science, measurements have been made of the chlorine and bromine contents of the saturated, polar, and aromatic fractions resulting from the ASTM D2007 clay-gel separation of various lubricating oils.

The dynamic range of the measurements can be from the ultratrace to the major constituent levels. The measurement reliability demonstrated in the basestock consistency work is ±3 percent (2σ) relative uncertainty over a twelve month period. Since the technique is generally non-destructive for elemental composition, the sample can be available after analysis for further measurement by this or other methods. Since the technique is nearly matrix-independent and does not depend on the chemical species or on physical properties such as viscosity, density, opacity, etc., it is well-suited for the fractionation work. In summary, the increasing need for accurate, sensitive, and unambiguous analyses of each of the halogens in organic liquids has prompted the development of optimized activation analysis techniques. The extension of this work to aqueous and other liquids will broaden its impact beyond the important area of oils and liquid fuels.

Reference

[1] Frassa, K. "ASTM/NBS Base Stock Consistency Study," NBS Spec. Pub. 584, p. 105 (1980).

R. F. Fleming

11. The Determination of Trace Elements in Biologicals and Injectables

A variety of biological and injectable product types are prepared and used in the diagnosis, prevention, or treatment of hypersensitivity to such factors as plants, pollen and food. As part of an extensive effort to establish accurate baseline data to define the normal trace metal levels for the variety of biological and injectable materials currently in use, a survey of 86 injectables of different types has been completed. The biological products or injectables included such materials as house dust, plasma, normal serum, whole blood, meningococcal polysaccharide, yellow hornet and honey bee venom, and tetanus, cholera, typhoid, rabies, and poliomyelitis vaccines.

Since the concentration of the 11 trace elements chosen for study was expected to be near the detection limits of atomic absorption spectrometry (AAS) with electrothermal atomization, special chemical and instrumental procedures were developed. The samples, stored under refrigeration, were first allowed to come to ambient temperature. The sealed cap of each sample vial was then removed in the plus 100 laminar flow clean room facilities in CAC. Samples in the form of solids or powders were reconstituted as directed. If the volume of the reconstituted samples was less than 15 mL, samples from vials of the same lot were combined in a clean Teflon beaker. The samples were placed in a hood and NBS purified acid was added. Digestion was carried out on a hot plate and the resulting solutions were evaporated to approximately 1 mL. These solutions were cooled and transferred to suitable volumetric flasks. The samples were then transferred to clean polyethylene bottles prior to analysis. If the samples became cloudy on dilution with water, they were redigested with HNO_3, and the final acid concentration adjusted to 20 percent HNO_3. This high acid concentration was found to stabilize the most difficult vaccine or plasma sample.

Biological matrices which have a relatively high concentration of Na, Ca, or Mg are known to produce interelement effects on most analytes when using electrothermal atomization with a graphite furnace. Graphite is a porous material that is easily penetrated by liquids and gases. Coating the graphite tube with a thin layer of pyrolytic graphite greatly reduces the effects of porosity and increases the sensitivity for some analytes. In addition, interelement effects are further reduced by matrix modification and the application of the L'vov platform, a small graphite platform placed inside the absorption cell. This platform reduces analytical interferences by allowing volatilization of the sample into a higher gas temperature than is possible without it.

The analytical results obtained for these materials are summarized in Table 9. Since similar SRM's were not available, the method of single standard addition along with close bracketing of unknowns with standards was used to check the recovery of the analyte. The results of this study will be used to develop candidate reference materials having suitable matrix characteristics and requisite trace metal compositions. When characterized, these standards will serve as a control or quality assurance standards for the determination of trace metals in biological and injectable materials.

Table 9. Concentration Range of Trace Elements in FDA Biologicals and Injectable Materials.

Element	Concentration Range, μg/mL
Al	0.02 - 250
As	<0.01 - 0.6
Ba	<0.01 - 1.0
Cd	<0.005 - 0.04
Co	<0.003 - 0.04
Cr	<0.005 - 0.2
Hg	<0.001 - 45
Pb	<0.005 - 0.5
Se	<0.01 - 0.1
Tl	<0.02 - 0.06
Zn	<0.05 - 50

Reference

[1] Dean, J. A.; Rains, T. C. Flame Emission and Atomic Absorption Spectrometry, Vol. 3, Elements and Matrices, Marcel Decker, 1975.

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12. Application and Evaluation of High Sensitivity Mass Spectrometry for Isotopic and Elemental Abundance Measurements of Uranium and Plutonium

The certification of materials for low-level or ultra-trace 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 ultra-trace components from complex materials. Under clean room conditions, it is possible to separate an element from a few milligrams of starting material and to determine the isotopic composition and elemental concentration with a high degree of accuracy. The feasibility of high accuracy measurements at the ultra-trace level has been demonstrated for the elements U and Pu using new and innovative microchemical procedures coupled with high sensitivity isotope dilution mass spectrometry (ID/MS). Two recent applications which clearly demonstrate the capability of this technique are a round robin exercise to determine the isotopic composition of nanogram quantities of U and Pu and the determination of U in Bovine Liver, SRM 1577a.

Research has been conducted at NBS as well as laboratories in the nuclear industry to develop the ability to analyze accurately and precisely nanogram quantities of U and Pu for isotopic composition. These data are essential to account for Pu and U throughout the nuclear fuel cycle and to detect diversion if it should occur. The resin bead technique in which several nanograms of both U and Pu have been extracted from dilute reactor dissolver solutions provides the matrix for physical transport from reactor to laboratory and is directly analyzable by mass spectrometry. To assess the state-of-the-art for high sensitivity mass spectrometry in the nuclear community, resin beads containing U and Pu separately, as well as both U and Pu were prepared, distributed, and analyzed as part of a "round robin".

The results for one of the low level uranium unknowns containing $^{238}U:^{235}U:^{233}U$ about 10:1:1 can serve to illustrate some of the information gained. A minimum of four replicate measurements were made of this sample by each laboratory with an average precision of 0.12 percent for the $^{235}U/^{238}U$ ratio and 0.25 percent for the $^{233}U/^{238}U$ ratio (1σ of mean). The relative standard deviations of the means (measured by the six participating laboratories) were 0.18 percent and 0.26 percent for the $^{235}U/^{238}U$ ratio and $^{233}U/^{238}U$ ratio, respectively. If the measured $^{233}U/^{238}U$ ratio were used as an internal standard to correct the $^{235}U/^{238}U$ ratio for fractionation, the σ_m of the latter ratio is substantially reduced to 0.05 percent. This suggests that the primary cause of intralab and interlab variation is lack of control of isotopic fractionation. The results reported here using nanogram samples are comparable with those reported in the more extensive round robins, IDA-72 and SALE, where microgram samples were analyzed using triple filament thermal ionization and Faraday cup detection.

The expertise gained from resin bead research and measurements has been applied to the determination of U in SRM 1577a, Bovine Liver (freeze dried, powder form). This sample was chosen because it contains one of the lowest U contents (∿700 pg/g) of any biological SRM. Because U is a biotoxin, 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 for the determination of picogram quantities of U by isotope dilution mass spectrometry using artifically produced ^{233}U (SRM 955) as a spike.

Typically 0.5 g of liver was decomposed using nitric and perchloric acids. The U in an aliquot of known weight containing 0.1 - 0.2 g equivalent of liver or about 100 pg ^{238}U was chemically purified on two small anion exchange columns. The chemically separated U is loaded onto a single anion bead which is transferred to a rhenium v-shaped filament and loaded into the mass spectrometer. The ionization efficiency for U loaded in this manner is about 0.2 percent. Therefore, 100 pg ^{238}U will yield an ion current of 10^4 ions per second for several hours which is sufficient for 0.1 percent precision.

However, the fundamental limitation on accuracy and precision is the magnitude and uncertainty in the chemical blank. Note that to determine 100 pg of U to an accuracy of 1 percent requires the variability in the blank to be less than 1 pg or 2.5 x 10^9 atoms ^{238}U. The chemical blank consists of U which is not indigenous to the sample. It can be considered as arising from three sources, each of which must be evaluated separately: 1. Dissolution blank - includes U from reagents and container (60 mL Teflon beaker) used for dissolution; 2. Column blanks - includes U from reagents, resins, and quartz ion exchange columns; 3. Loading blank - includes U from the source that is indigeneous to the bead and filament material. Four loading blanks were determined and ranged from 12-40 femtograms ^{238}U. Single determinations were made on all reagents used in the chemical separation. The total U added to the chemical separation from these sources is 2.5 pg. Since 0.5 g of sample contains about 350 pg of ^{238}U, the contribution from this blank is less than 1 percent. The major source of blank is the column blanks because aliquots of 0.1-0.2 g of sample or about 100 pg ^{238}U are passed through the chemical separation. Ten column blanks have been measured and ranged from 2.4-5.2 pg.

Figure 14 is a graphical representation of U determinations on SRM 1577a. The figure illustrates four important points: (1) Duplicate determinations on a single aliquot agree within the stated uncertainty which is typically 1.5 percent; (2) Aliquots of different sizes agree within the stated uncertainties indicating that the chemical separation and mass spectrometric procedures as well as the data reduction are valid; (3) All determinations agree within the stated uncertainties indicating SRM 1577a is homogeneous to about 1 percent for 0.5 g samples; (4) Small quantities of U ($\sim 10^{11}$ atoms ^{238}U) can be chemically separated in high yield and determined by pulse counting with an overall uncertainty of about two percent.

As can be seen from the extensive effort to identify and measure the sources of blank for analysis of Bovine Liver, clean and efficient chemical separation procedures are necessary. In addition, the mass spectrometric analysis requires extreme care in the prevention of contamination and an understanding of the nature of isobaric interferences and their prevention as well. The need to determine picogram quantities of critical elements in small samples of organic and inorganic materials will undoubtedly increase in the near future since their presence can markedly alter both chemical and physical properties and affect the biochemistry of plants and animals. The techniques described in this report should be applicable to other elements with comparable success.

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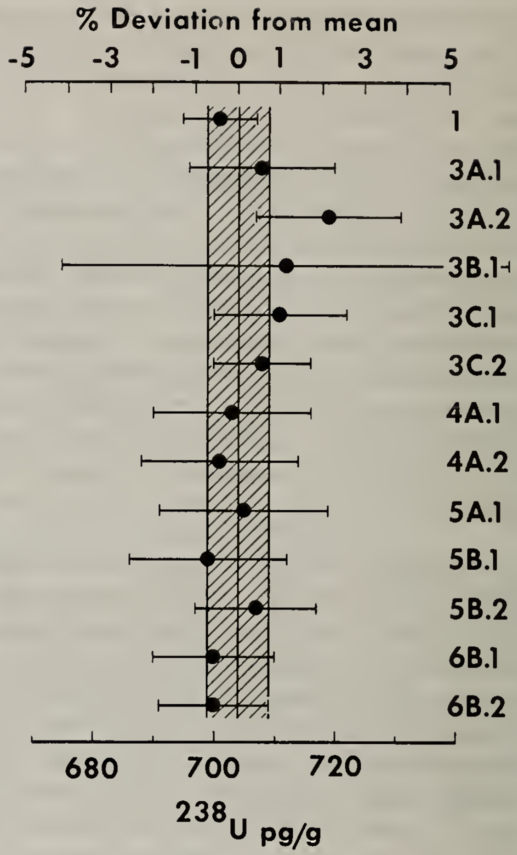
Figure 14. Graphical representation of concentration data. Dots represent a single determination and its associated error (2σ). Legend on right indicates bottle number, letter denotes aliquot, and decimal number denotes replicate determination on aliquot. The middle vertical line represents the mean of the mean values for all samples, which is 703.8 and the outer lines represent $2\sigma_m$, which is 4.3 or 0.61 percent.



13. Development of Improved Matrix Modifiers for Use in Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is a widely used analytical technique for the determination of metallic elements. Since AAS is a relative technique, a quantitative determination can only be carried out by comparison to a reference solution. If the behavior of the sample is different than the reference solution, it is implied that there is an interferent. Depending upon the cause, the interference can be classified as chemical, physical, background or spectral. While background and spectral interferences are based on the measurement of non-specific signals, chemical and physical interferences have an influence (positive or negative) on the total number of atoms formed per unit volume of the absorption cell. The most common interferences encountered in the analysis of biological tissue, environmental samples or food samples are of the chemical variety. The interferences encountered in flame sources for the production of atomic vapor in AAS are generally understood and methods have been developed to alleviate them. However, in electrothermal atomization, the process is not clearly understood and severe interference effects are encountered. Since the concentration of many analytes are below the detection limits of flame AAS, electrothermal atomization is used routinely because of its increased sensitivity.

In electrothermal atomization, controlling the sublimation of the analyte during the processing step is of major importance. Since the atomization of a sample in a graphite tube furnace can only take place from the graphite surface, it is essential that the sample remain in intimate contact with the hot graphite surface for as long as required for complete atomization. In contrast to flame AAS, the formation of sulfate, phosphate or oxides in the graphite tube is often advantageous.

A number of publications have described matrix modification procedures by which analyte losses during the preatomization stage with electrothermal atomization may be minimized or eliminated [1-3]. In general, the methods developed are for specific analytes and matrices. The absorption signals for Al, As, Be, Cd, Co, Fe, Ni, Pb, Sb, and Se in AAS with electrothermal atomization are severely suppressed in matrices that contain relatively high concentrations of Na, Ca, and/or Mg (e.g. human tissue or serum). This suppression has been observed to be as high as 100 percent for Cd and Pb in 1:5 aqueous dilutions of sera.

In an attempt to minimize or eliminate analyte response suppression, a series of experiments was conducted to evaluate HNO_3, HCl, $HClO_4$, H_2SO_4, H_3PO_4, $K_2Cr_2O_7$, ammonium orthophosphate [$(NH_4)_2HPO_4$], and ammonium sulfide as matrix modifiers. In general, a one percent nitric acid solution was found to give the best precision and accuracy when the total solids in the samples were low. A one percent solution of $(NH_4)_2HPO_4$ and HNO_3 was the most efficient matrix modifier for Cd, Co, Fe, Pb, and Ni in a variety of matrices. Several series of solutions of low alloy steels (SRM's 364 and 1269) were prepared with and without a one percent solution of $(NH_4)_2HPO_4$. Lead recoveries of 100 percent were obtained from solutions with phosphate present while only 50 percent recovery was obtained from solutions without phosphate. Matrix modifiers which have been found to alleviate the largest number of interferences in AAS with electrothermal atomization are listed in Table 10. While phosphate was found to alleviate interferences for many analytes, it was found to have an adverse affect on As analyses. A similar effect was observed for Se.

While a universal reagent for matrix modification in AAS has not been found, the knowledge obtained in this study has led to an improvement in the precision and accuracy of the analysis using AAS of trace elements in a wide variety of materials. Presently, a study is underway to evaluate the effect of combining $(NH_4)_2HPO_4$ with various organic compounds as a new approach to improved matrix modification.

References

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T. A. Butler, T. C. Rains, T. A. Rush

Table 10. Matrix Modifiers for AAS with Electrothermal Atomization.

Analyte	Materials	Matrix Modifier
Cd, Pb	Natural Waters Leachates Human Tissue and Serum Ores Air Particulates FDA Injectables	1% Solution of $(NH_4)_2HPO_4$
Fe, Ni, Co	Au Stripping Solution Human Serum FDA Injectables	1% Solution of $(NH_4)_2HPO_4$
As, Se	All Materials	1000 µg Ni/mL
Al	Human Tissue and Serum	0.5% H_2SO_4
Be	Natural Waters	25-50 µg Ca/mL
Sb	Air Particulate	1% Solution of $(NH_4)_2S$
Sn	All Materials	10% HCl

14. Development of Silica-Gel Procedures for the Analysis of Trace Quantities of Copper and Nickel

In recent years, the need to accurately determine elements at trace level concentrations in environmental, biological, and industrial samples has become critical. As a result, a number of isotope dilution procedures, which were once considered to be state-of-the-art, have become obsolete. This was the case for the procedures used for the determination of copper and nickel. Both procedures required large amounts of sample while yielding low to moderate signal intensities, thus limiting the sensitivity of the measurement. In addition, the chemical separation procedures which had been used to prepare the samples yielded blanks which were sufficiently large and variable to cause significant error at the sub-microgram level. The need to determine nickel in human liver samples for the National Environmental Specimen Bank ultimately led to the development of improved analytical procedures for both nickel and copper. The nickel was separated from the matrix elements by electrodeposition from ammonical solution, instead of by the previously used dimethylglyoxime solvent extraction procedure, which led to a three-fold reduction in the analytical blank. The mass spectrometric sample mounting procedure utilizes a single filament silica gel technique. This procedure, which involved drying sequential layers of silica gel, sample, and phosphoric acid onto the surface of a platinum filament, was a direct outgrowth of the method developed for the determination of the atomic weight of silver. The basic sample mounting procedure was followed by a high temperature drying step where the filament temperature was rigidly controlled by use of an optical pyrometer.

During the analysis of nickel in human liver, it was observed that the small amount of copper which remained after the separation gave an intense ion beam. Slight modification in both the sample mounting technique and the analysis procedure, led to a new silica gel procedure for copper which yielded a four-fold increase in signal intensity with a twenty-fold reduction in sample size.

As a result of this research, the elements copper and nickel can be determined at the submicrogram level with improved accuracy. This increase in both sensitivity and accuracy can now be used to facilitate the determination of these elements in Standard Reference Materials, as well as in the large number of other standards and samples which require the analysis of trace quantities of copper and nickel.

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15. Research to Develop High Accuracy Coulometric Assay Methods for Uranium Metal and Uranium Oxides

Over the past few decades, accurate analysis of uranium metal and uranium oxides (mainly U_3O_8) has assumed great importance. The nuclear reactor industry requires accurate assays of uranium metal in reactor fuel rods, while fuel rod manufacturers who handle isotopically enriched, and therefore very expensive material, require accurate assays of U_3O_8. Nuclear waste management and radiation public health regulations mandate accurate accounting and radiation fuel mass balance, which in turn necessitates accurate analyses of uranium. For its part, the National Bureau of Standards has issued Standard Reference Materials of certified purity (SRM 960 Uranium Metal and SRM 950 Uranium Oxide) to assure measurement comparability and traceability both nationally and internationally. Considerable research has been conducted at NBS to improve the methods of uranium analysis to better meet the more exacting demands imposed by industry, government, and society at-large.

In the last ten years, a controlled-current coulometric method for uranium assay, based on electrogeneration of titanous ion at a platinum cathode with subsequent reduction of uranium(VI) to uranium(IV) has been developed and refined at NBS. This past year, a major effort was launched to investigate and correct the deficiences of the method which have limited the precision of the assay to about 70 parts per million (relative standard deviation). These deficiences include electrode poisoning, current inefficiences, and slow rates of reaction.

To gain a clearer understanding of electrode poisoning and the resultant loss of current efficiency, a detailed study of the electrogeneration of titanous ion in several electrolytes using different electrode materials was undertaken. Plots of current density versus electrode potential were constructed from which the current efficiency was computed. The effects of electrolyte composition and electrode material on the reaction rate of uranium(VI) with titanium(III) were also monitored.

This research has led to the development of a new procedure for the coulometric assay of uranium using a mercury-pool cathode and a supporting electrolyte containing 9 mol/L sulfuric acid and 0.2 mol/L titanyl sulfate. With this procedure, one gram samples of uranium have been titrated with a precision and accuracy of 30 parts per million (relative standard deviation). This represents a considerable advance over the previous coulometric procedures and offers distinct advantages over the Davies-Gray procedures in the form of smaller sample size by a factor of two to three, increased precision, and fewer operations. Furthermore, the coulometric method is absolute, based directly on the Faraday constant, and not tied to other chemical standards. Work is continuing to refine further the procedure with particular attention being paid to identifying a catalyst to increase the rate of reaction near the equivalence point of the titration.

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16. Development of a High Precision Method for the Assay of Milligram Samples of Uranium

For more than twenty years, NBS has maintained a set of 18 uranium isotopic SRM's which cover in detail a 235/238 isotopic ratio range from less than 0.01 to approximately 200. In this respect, the uranium isotopic SRM's are unique and are utilized both nationally and internationally to calibrate instrumentation for the elemental and isotopic assay of uranium in the nuclear fuel cycle. The current level of certification for the major isotopes of these materials is inadequate for present and projected nuclear safeguards requirements. A primary obstacle to improving the accuracy of these materials has been the inability to assay mg quantities of highly enriched or depleted separated isotope solutions which are then utilized to prepare standards of known composition for instrument calibration.

The goal of this research project was to develop a method for the high precision assay of 25-100 mg of uranium (separated isotope solutions) by a modified Davies-Gray titration technique. Under normal conditions, the Davies-Gray is capable of high precision/high accuracy assay of 5 in 10^5 (1 standard deviation). However, to achieve this level of precision, at least 2-3 g of material is required for each analysis. Since large quantities of uranium separated isotopes are expensive, scarce, and in some cases, a radiation hazard, there is an acute need to develop a high precision assay utilizing less than 100 mg of sample per analysis. When this work was initiated, no method existed which was capable of yielding an uncertainty less than 0.01 percent for measurements on a sample of less than 100 mg.

A manual titration procedure has been developed, employing essentially the same techniques as the standard Davies-Gray titration. However, the precision of this new method, for a 100 mg sample, is nearly as good as would be determined from a two to three gram sample by the conventional method. Alternatively, samples of 10 mg or less might be titrated to the 0.05 percent precision level of the standard Davies-Gray titration. The usefulness of such an improvement in sample size requirement is obvious but equally important are the facts that no significant changes in equipment and chemistry are required.

These improvements were achieved through the methodical study of the effects of various parameters upon the titration and through the application of improved techniques to the basic method. The more significant changes are briefly described and explained below. First, a more stable and more sensitive digital millivolt meter was substituted for the conventional pH meter for end-point indication. Second, blanks and titrations were studied as a function of total reagent volumes and, as a result, a miniaturization of the titration was achieved with minimum inconvenience and maximum benefit (end-point sensitivity). Improved methods of dichromate reagent addition were developed to assure accuracy in the consumption of this primary standard titrant. The result of these and other improvements is a weight titration using 1/2 scale of all normal reagents. For samples of 100 mg, within set precisions of better than 0.006 percent have been achieved.

The initial objective of this research, a highly precise assay capable of assaying milligram quantities of uranium in separated isotope solutions, has been accomplished. Although a consistent bias of -0.09 percent is observed for a sample size of 25-150 mg, this will not hinder the preparation of accurate calibration standards from two master solutions of uranium separated isotopes. With the potential for preparing more accurately known standards, it is now possible to make measurements which will lower the uncertainty in the certification of the uranium isotopic SRM's to a level which addresses the needs of the nuclear industry. With additional research, the method could be modified to eliminate the bias. Either a modified method or the high precision method shows promise as an alternate method for routine assay of uranium in the nuclear fuel cycle. The widespread use of such a method to replace the more classical Davies-Gray titration would conserve the large amounts of uranium that are now expended for assay purposes.

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17. Research to Develop ID/MS for Trace Concentrations of Vanadium

There have been few SRM's certified for vanadium due to the extremely low levels of this element in most natural, biological and environmental materials (excluding fossil fuels). Many cases of vanadium toxicity have been reported as connected with the use of fossil fuels [1]. It is significant that the most concentrated natural sources of V are fossil fuels such as oil and coal; in oil, it is often the major inorganic component. Vanadium is also ubiquitous in industry in the form of ferro-vanadium alloys or other species used in dozens of processes as the major catalyst. The development of an isotope dilution mass spectrometric (ID/MS) procedure to analyze vanadium will enable NBS to certify this important element in a large variety of requested materials.

The first high accuracy measurement of vanadium by ID/MS was completed during the year on proposed SRM 1634a, Trace Elements in Fuel Oil. The newly developed chemical and mass spectrometric methods were applied initially to this SRM because of its relatively high vanadium concentration (∿50 ppm). Future efforts will be directed at the ultra-trace level.

In developing the chemical procedure for determining vanadium by isotope dilution, extensive research to decontaminate the spike material (^{50}V) was necessary. The isotope obtained for the spiking was found to be unsuitable in its initial condition due to contamination by potassium and other elements. A separation technique was developed to purify the ^{50}V isotope which also was tested for the removal of isobaric interferences; specifically, the mass 50 isotopes of titanium and chromium.

Before precise isotope ratio measurements were made, a thorough investigation of the various modes of thermal ionization was completed. Studies of the ionization patterns and efficiencies of vanadium revealed distinct differences between several pretreatment methods and between different molecular forms. The final form chosen for loading the sample onto the mass spectrometer filaments was vanadium oxychloride; $VOCl_3$ is believed to be its major constituent. This is produced by final treatment with $HClO_4$ and HCl and filament drying with heat, in air.

The chemical separation of vanadium from other metals was based on formation of the peroxide complex and cation exchange chromatography. The peroxide complex prevented the ion exchanging of vanadium while reducing chromium to its trivalent state which was bound as were the other metals by the ion exchange column. The chemical separation, sample preparation and final vanadium species adjustment were done under Class 100 clean room conditions. This procedure was found to produce blanks below 1 ng while eliminating the chromium and titanium present at comparable concentrations. During this separation, approximately 20 specific elemental components, present at lower concentrations in the fuel oil matrix also were removed. A series of oxidative steps, employed as a pretreatment, resulted in a sample having uniform characteristics for mass spectroscopic analysis.

The mass spectrometry procedure developed for vanadium employs a rhenium triple filament ion source. Approximately 1 µg of vanadium supplied as the oxychloride in 10 percent hydrochloric acid is dried onto each of the two sample filaments. The vanadium is then heated in air to approximately 750 °C to convert it to a black oxide (probably VO_2 or V_2O_3). A major effort has been required to minimize the isobaric interference at mass 50 resulting from chromium. Chromium is present in the mass spectrometer source components and in the rhenium filament material. The chromium background for vanadium analyses has been reduced by more than an order of magnitude during the past year. Among the techniques used to reduce the chromium background are: use of zone refined rhenium which is acid leached prior to filament fabrication, and use of tungsten posts to hold the filaments rather than the normally used stainless steel. Although initial vanadium measurements have been at relatively high concentrations, the sensitivity of the technique will allow high accuracy determinations of vanadium concentrations at the sub-ppm level. This is particularly important in view of the discrepant data which has appeared in the literature in recent years regarding the concentration of vanadium in botanical and environmentally related materials.

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J. W. Gramlich, H. M. Kingston

18. Investigation of Ionic Chromium Speciation

Chromium is present in a wide variety of materials, including plants and minerals, industrial metal products, and waste effluents. It is an important trace metal that is both essential and toxic, depending on its valence state and concentration [1]. Consequently, its determination has been a subject of continued research for several decades.

Since studies have established that the trivalent form of chromium is relatively harmless and that the hexavalent form is toxic, special efforts have been undertaken to distinguish between the two valence forms of chromium present in food and water. Anion exchange chromatography has been used to separate Cr(III) from Cr(VI); AAS then was used to measure Cr(III) in the column effluent [2]. Total chromium was measured by AAS in a portion of the sample that had not been passed through the column and Cr(VI) then was determined by difference [2]. Solvent extraction has also been used to separate Cr(III) and Cr(VI). Ammonium pyrolidine dithiocarbamate (APDC) is used to chelate Cr(VI) and the complex is then extracted into methyl isobutyl ketone. Atomic absorption spectrometry was used to determine Cr(VI) in the extract [3]. Chromium(III) can be coprecipitated from water samples with Fe(III) hydroxide. In another method, Cr(VI) is separated by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. Numerous other analytical techniques, yielding limited success, have been described in the literature [4].

With the increased interest in ionic chromium speciation shown by the Office of Standard Reference Materials and the Office of Environmental Measurements, an evaluation of several analytical techniques for determining Cr(III) and Cr(VI) was undertaken. The first technique studied was an anion exchange procedure. The aqueous samples were made 1 mol/L in HCl and then introduced onto a gravity-flow column. The Cr(III) was eluted from the column with 1 mol/L HCl while the Cr(VI) was adsorbed. After the Cr(III) was eluted from the column, a solution of 0.01 mol/L ascorbic acid in 0.01 mol/L HCl was added to reduce the Cr(VI) to Cr(III) directly on the column. The newly-formed Cr(III) species was then eluted from the column and AAS was used for online detection of Cr(III), now representing the Cr(VI) content.

Since the direct measurement of Cr(VI) is of major interest, a study was conducted using Chelex 100 resin. In the initial study, 50 μg of Cr(VI) and 50 μg of Cr(III) were transferred to a beaker and the pH of the solution adjusted to 5 with pH 5.5 acetate buffer. The solution was transferred to a 1x7.5 cm ion-exchange column containing Chelex 100 resin, 200-400 mesh size (sodium form). Water was added to the column and 10 mL portions of the effluent were collected. Each test portion was then analyzed for Cr by flame AAS. After the Cr(VI) was eluted, the eluent was changed to 3 mol/L

HCl to elute the Cr(III). Complete recovery of Cr(VI) was obtained in 50 mL of eluent while Cr(III) showed extensive tailing with 95 percent recovery after collecting 70 mL of effluent. Since our interest is Cr(VI) at the nanogram level, the experiment was repeated using 50 ng of each of Cr(VI) and Cr(III). The analysis of the effluent was made by AAS with electrothermal atomization. With these nanogram amounts, the Cr(VI) was completely eluted in 25 mL of effluent with no detection of Cr(III).

The utility of the procedure was evaluated using two leachate samples from solid waste and two samples of water taken from the pond located on NBS grounds. Each sample was analyzed as described. No Cr(VI) was detected in any of the samples. The experiment was repeated after each sample was spiked with 25 ng of Cr(VI) and allowed to stand for 12 hours. The recovery of Cr(VI) from the pond water varied from 0 to 30 percent with recoveries of 70-80 percent from the leachates. This result, coupled with the total recovery of Cr(VI) in the last experiment, suggests that Cr(VI) is being reduced by species present in the water. Additional studies are being planned to determine the stability of Cr(VI) in various types of aqueous media.

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B. E. McClellan, J. D. Messman, T. C. Rains

19. Transfer and Analysis of Inductively Coupled Plasma (ICP) Emission Data Using a Mini- and a Main-Frame Computer on the NBS Data Network

Two major sources of systematic error in the ICP technique can limit the accuracy of analyses. The first is spectral interferences which are caused by spectral line overlap, and the second is matrix effects which are caused by the presence of various constituents in the sample itself. Approaches to minimizing and correcting for these effects have been developed in this laboratory. However, they cannot be immediately put to use without improved computing capability. Spectral line selection requires the use of the ICP minicomputer and microphotometer which is located outside of the ICP laboratory. Data acquisition for the matrix effect studies is accomplished by the ICP minicomputer, but the analysis and result calculations are most efficiently handled by the NBS main computer. In both cases, communication links and protocols had to be developed to enable remote usage of the ICP minicomputer and data transfer to the NBS main computer.

The procedure for identifying and selecting spectral lines involves the examination of a photographic plate on the microphotometer. This instrument has been modified to provide linearly encoded distance measurements in order to characterize the spectral plate dispersion. Lines of known wavelength are paired with their respective plate positions. A parabolic-fitting program is used to calculate the plate dispersion. New line positions can then be used to calculate unknown wavelengths or unknown line positions can be calculated for known wavelengths to identify intended analysis lines. The interactive nature of this process made it necessary to establish multi-user capability on the minicomputer and to provide a remote terminal at the microphotometer. This was accomplished by installing an additional interface board in the computer and connecting both the interface and the remote terminal to the NBS Data Network.

The existence of matrix effects in the ICP technique has been recognized in this laboratory and steps have been initiated to eliminate or reduce them. Their presence is significant when applying the technique to the high-accuracy analysis required for the certification of Standard Reference Materials. In order to characterize the extent of matrix effects for ten elements in a typical sample, the experiment would generate 5,000 raw data points and require 2,500 calculations for each matrix type. The best approach to analyze such a data set is to use the OMNITAB package which is supported on the NBS main computer. During the experiment, data are automatically stored on the ICP minicomputer data disc. Transfer of these data from the disc to the NBS main computer involved extensive software development to connect the two computers on the NBS Data Network. The connection actually employs the NBS microcomputer as an intermediate device for temporary data storage.

Both the line identification and the matrix effect experiment take approximately one-third the time previously required. Furthermore, incidences of error in line identification and calculation have been virtually eliminated. These steps in interactive computing and data analysis have greatly increased the efficiency of the set-up procedures for ICP simultaneous multielement analysis.

R. L. Watters, Jr.

20. Evaluation of Sources of Error in D.C. Plasma Spectrometry

The Direct Current Plasma (DCP) is a relatively new analytical emission source in the Division. Within a relatively short time span, this source, in combination with an echelle spectrometer, has been applied to trace element determinations in a variety of complex matrices in support of programs such as Nuclear Waste, Recycled Oil, and Standard Reference Materials. In addition to this analytical role, research has been conducted to evaluate the factors that influence precision and accuracy for the purpose of developing improved instrumentation and analytical methodologies. Most of this research has concentrated on studies of noise (which affects detection limits and precision) and interferences (which affect accuracy).

A study of some twenty elements has indicated that detection is limited, under the high spectral resolution conditions used, by a combination of photomultiplier dark current noise and plasma background emission flicker noise. These are fundamental limitations meaning that improved detection limits can be most simply obtained by increasing signal strength rather than reducing noise.

Precision at high concentrations (at least two orders of magnitude above the detection limit) is defined by analyte emission flicker noise resulting from the sample transport system along with any temperature or vibration-induced wavelength drift of the spectrometer. We have somewhat reduced wavelength drift through thermal stabilization of the spectrometer.

As a consequence of these studies, it is clear that the most direct method to improve detectability and precision involves improvement of sample transport efficiency and stability. To this end, alternate sample introduction systems, including ultrasonic nebulization and discrete sample injection, are being investigated.

Additive interferences resulting from spectral line overlaps and multiplicative interferences, produced by elemental interactions in the plasma excitation volume, have proven to be the major limitations to analytical accuracy in that they both influence the relationship of standard and sample emission intensities. Spectral line width studies of the DCP indicate that the echelle resolution, using the minimum slit width available, provides the optimum spectral discrimination possible (i.e., the half-widths of broadened spectral lines are approximately the same as the minimum spectral bandpass of the echelle). This means that further improvement in spectrometer resolution is useless and that reduction of spectral interferences must be based on refinement of background-correction techniques.

Studies of multiplicative interferences resulting from interelement effects in the DCP present an extremely complex picture, with interferences being dependent on the observation area as well as the identity of the interacting elements. Buffer solutions, such as lithium chloride, have proven to be of some use in the reduction of interelement effects, but their effect appears to be highly dependent on acid concentration. The result of this study has led us to the use of a procedure combining matrix-matching of acid concentration, a lithium buffer (1000 µg/mL), and single-point standard addition.

The recent acquisition of two multielement cassettes has directed our studies towards problems in the application of the DCP to simultaneous multielement analysis, the eventual goal being the development of a system capable of high accuracy work. The primary problem which must be overcome is the detection and correction for spectral interferences on a multielement basis.

C. G. Blundell, M. S. Epstein

21. Research to Develop Acid Rain Reference Materials

Within the last decade, the phenomenon of acidic precipitation has attracted increased attention both on the national and international fronts. The Inorganic Analytical Research Division, primarily in support of the United States Environmental Protection Agency and the United States Geological Survey, is taking an active role in the study of acid rain. This effort has focused on analytical chemistry to ensure quality assurance, measurement comparability, and consistency throughout the nation. Since 1975, NBS has prepared and analyzed four series of reference materials to be used for the chemical analysis of natural precipitation samples. These samples have provided a means of intercalibrating atmospheric monitoring stations. These solutions are also being monitored for stability, primarily with regard to pH and conductivity. To improve the stability, alternatives to the present use of glass ampoules for the storage of these solutions are being investigated. In addition, research is being conducted to improve the measurement of pH and acidity in low conductivity, unbuffered solutions, such as encountered with acid rain.

In the past year, investigations have revealed serious problems in the measurement and subsequent interpretation of pH in acid-rain-like solutions. It is well known that the customary arrangement for measuring pH (glass/reference electrodes) measures not a single quantity (i.e., hydrogen ion), but rather a sum of potentials. The "unwanted" potentials include asymmetry potentials, liquid junction potentials, streaming potentials, and several others related to the non-ideal behavior of the solution and of the electrodes. Insofar as these potentials are constant between standards and unknowns, they can be electronically offset and therefore, cause no major problem. Such is not the case in acid rain solutions which are unbuffered and low in ionic strength. Data have been obtained revealing residual liquid junction potentials which can easily bias the pH reading by 0.1. Because of this bias, fundamental interpretation of the pH number of such solutions in terms of hydrogen ion is totally impossible.

In a related way, the measurement of total acidity, in solutions of extremely low acidity, is beset with potentially serious errors. Experiments indicate that these errors result from a combination of the manner in which the end-point is determined and the effects of dilution.

The impact of these findings is clear; the discipline of analytical chemistry has not kept up to the demand in regards to this far-reaching environmental phenomenon. Research is underway to develop new standards and measurement protocols intended to ensure measurement quality and comparability, as well as to gain a better understanding of the problems encountered in the measurement of pH and acidity in acid rain solutions.

W. F. Koch, G. Marinenko, J. W. Stolz

22. Design and Implementation of a Solid State Filament Control for Thermal Ionization Mass Spectrometers

Precise and accurate isotope ratio measurements require the use of a highly stable and well-regulated supply of current to the thermal ionization ribbon filaments. The filament power supply and control unit which had been in use for many years utilized a set of Variacs in series to control the filament current setting. Although relatively simple, low cost, and capable of being AC-transformed near the source to maintain operator controls at ground potential, the unit had become the limiting factor in ion beam stability and was no longer adequate. In addition, maintenance was a constant problem and the design was not amenable to automatic or computer control. To improve overall performance, reduce down-time and maintenance, and provide facilities for computer control, a new triple filament power supply and control unit was designed.

The electronically regulated power supply contains three identical filament control circuits and is fully isolated to permit operation at the 10 kV ion source potential. Substantial circuitry is employed to provide protection from electrical transients generated by high voltage arc-over in the source housing. Vulnerability to arc-over transients is responsible for the failures of similar instruments designed for this purpose. Each circuit is current controlled to provide up to 7.5 amperes at a maximum voltage of 7.5 volts regulated to better than ±20 ppm typical stability. The current meters are autoranging for better readability at low filament current settings. Smooth manual control is achieved by using 10-turn potentiometers with a response tailored to enhance low range adjustments. Push-pull, on-off switches on each control simplify the front panel operation, and provision is included for future adaptation to digital control. Construction of the instrument is of a double box arrangement with no high voltage surfaces exposed in order to eliminate personnel shock hazard. The meters are viewable through a large ruby plexiglass face plate providing wide angle readability. Two of the three special high voltage isolation transformers recovered from the previously used circuitry are used in this instrument, eliminating a major cost item in its construction. The bulk of electronic components are located on easily replaceable modules. Three interchangeable meter-pot assemblies, a power heat sink assembly, and a control circuit board constitute the system. Modular construction of the electronics assures minimum down-time for repair when replacement subassemblies are available.

Three slightly different hand-wired versions of the control unit have been constructed and have been in use for almost one year. Essentially no problems have been encountered and the original performance specifications have been realized. Printed circuit boards have been designed to make the unit easy to assemble as well as to repair. Two of these have been constructed and installed and additional units are planned as replacements for the control units with Variacs.

The successful completion of this unit is an important step toward a fully automated mass spectrometer that will dramatically improve analytical efficiency and output.

I. L. Barnes, R. W. Shideler

23. Digital Control Modification for the Varian FR-41 Gaussmeter/Controller

A fully digital control system has been added to a Varian FR-41 magnet control unit to upgrade and enhance its utility and extend its useful life. To automate fully the operation of a mass spectrometer, complete computer control must be achieved for all components that function during the analysis. A key component of this control is the gaussmeter used to control the magnetic field. Currently, the gaussmeter is controlled by a combination of manual and computer controlled switching, and does not have the flexibility required for such operations as completely automated baseline measurement and isotope peak centering.

The system interfaces to a digital computer or desktop calculator from which a full five-digit number representing field gauss may be executed under program control. The system is comprised of a series of digital registers which receive a multiword sequence from the control medium and operate a series of analogue switches interconnected to the mechanical switches in the Varian unit. Control may be returned to the mechanical switches for off-line operation. The contact resistance reliability of the analogue switches is superior to that of the mechanical rotary switches and improves the reliability and stability of the gauss setting during digitally controlled operation. The unit is built on a circuit board installed within the Varian chassis. A separate five digit LED display panel is mounted on the front panel. The unit is a hand-wired first prototype and will be replaced by a much improved second generation design created to reduce construction and installation costs as well as further enhance system stability.

Implementation of this device, along with the other units leading to complete automation, will have a large impact on the efficiency of mass spectrometric analytical measurements. For many applications, the instrument operator will be free to perform other tasks and research.

I. L. Barnes, R. W. Shideler

24. Evaluation of a Collimated Ion Collector for Thermal Ionization Mass Spectrometry

One of the fundamental conditions for collecting and detecting charged particles is the suppression of stray electrons to the extent that the net gain or loss in charge is zero. For many years, the high accuracy mass spectrometers at NBS have been equipped with a 50 percent transmission grid in front of the final defining slit in the collector. The grid, typically a series of flat tungsten wires placed parallel to each other, was electrically isolated and attached to an auxiliary electrometer. This grid, in conjunction with a series of tungsten wire suppressor grids, was a very effective means of collecting stray electrons. This particular configuration has been utilized for 20 years of atomic weight research, the certification of all of the U and Pu isotopic SRM's, and for numerous trace element determinations by isotope dilution.

While useful and very effective for high accuracy measurements, this system did present several drawbacks. Among these were the loss of signal due to the transmission grid, and the increased ion scatter and electron production resulting from the ion beam striking the edges of the grid wires. With the increased pressure to analyze micro amounts of material at high accuracy and without major modification of the equipment, the loss of 50 percent of signal to the transmission grid became very critical. Therefore, research to develop an innovative system to collect 100 percent of the ion beam and also suppress electrons has some very definite advantages in the analyses of micro samples where the concentration of the analyte element is less than 1 µg/g.

An improved collector has been designed. The collector assembly, shown in figure 15, completely eliminates all grids in front of the final defining slit and utilizes a pair of identical slits, separated by 1.3 cm to collimate the beam, reduce scattering, and eliminate stray electrons. All screws or other protrusions on the front of the slit assembly have been replaced by small clips carefully placed to ensure that no part of the beam is intercepted. This modification virtually eliminates any source of "stray" electrons. The original deep Faraday cup ion collector and an electron suppressor plate (maintained at -90 V) have been retained. A modification of this collector has been designed with a movable Faraday cup. With this configuration, an ion counting detection system can be placed behind the Faraday cup, allowing for rapid change between large ion current measurements with a Faraday cup collector to ion counting detection of extremely small signals. In effect, the combination of the collimated ion collector, movable Faraday cup and ion counting detection system will increase by several orders of magnitude the useful signal intensity measurement range, for high accuracy analyses, of the NBS thermal ionization mass spectrometers. Two of the collimated ion collectors have been in routine use for nearly one year and have proven to be very satisfactory. The increased signal intensity has resulted in improved accuracy for elements with low ionization efficiencies and has allowed a reduction in sample size, without compromising analytical quality, for nuclear materials where the amount of material handled is an important health and safety consideration.

Several element spectra including Ca, Dy, Er, Ga, Pb, Sr, Tl, U, V, and Zn have been extensively examined using the new collector. A typical mass spectral scan for one of these, uranium, is shown in figure 16. As is shown, even with signals (235:236) differing by a factor of about 650 to 1, excellent peak shape is maintained, no evidence of "tailing" by the large peak is evident and no baseline disturbance by either scattered ions or electrons is detected. The measured signal is 100 percent larger than that obtained using the more elaborate collector with the same size sample at the same temperature. A recent, detailed examination of peak shape in a similar scan of a lead sample indicates that the "flat top" portion of the peak is "flat" to one part in 25,000, over 25 percent of the peak width, which is a significant improvement over that obtained with the old collector.

I. L. Barnes, W. A. Bowman, III, J. W. Gramlich

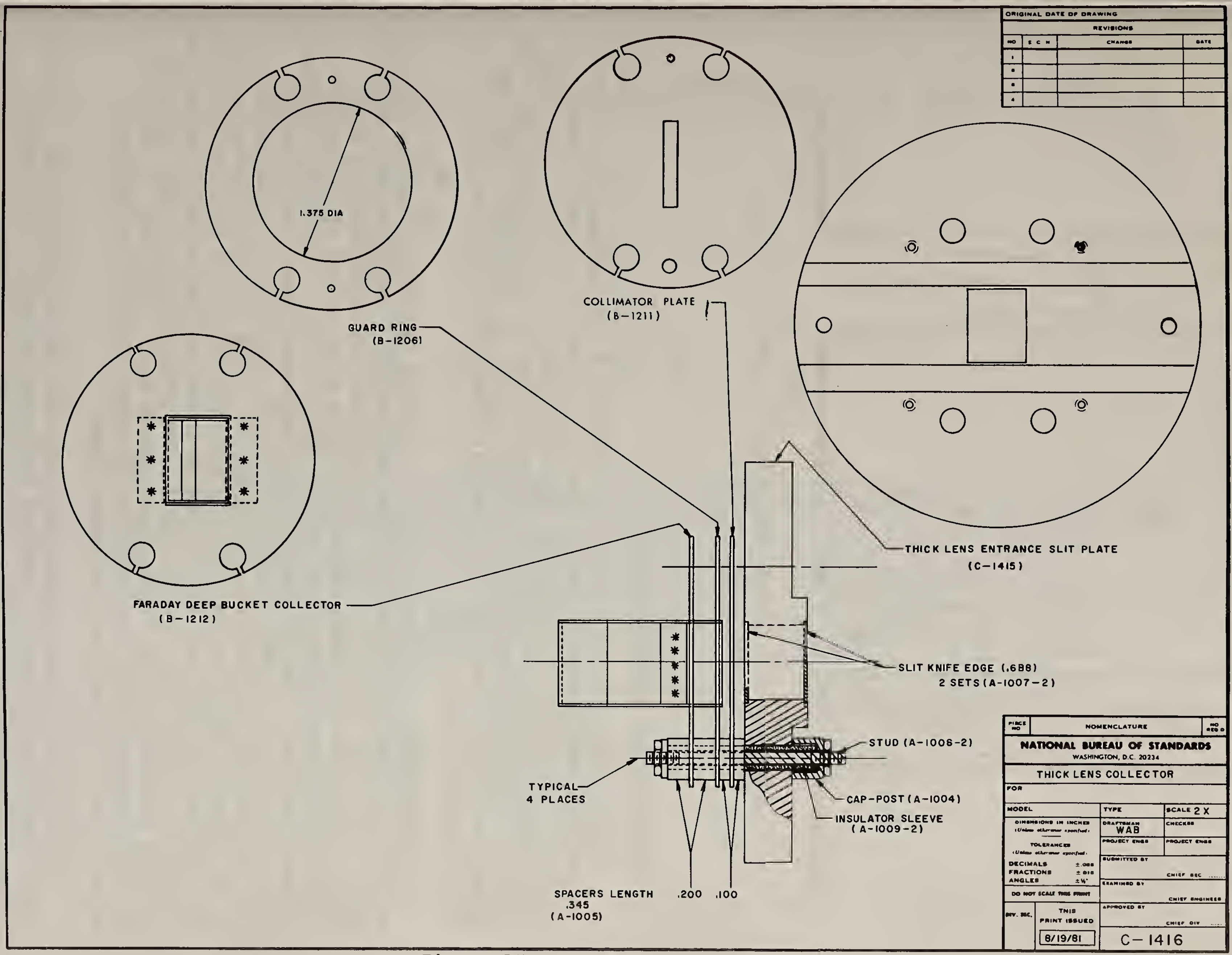

Figure 15. Thick lens collector.

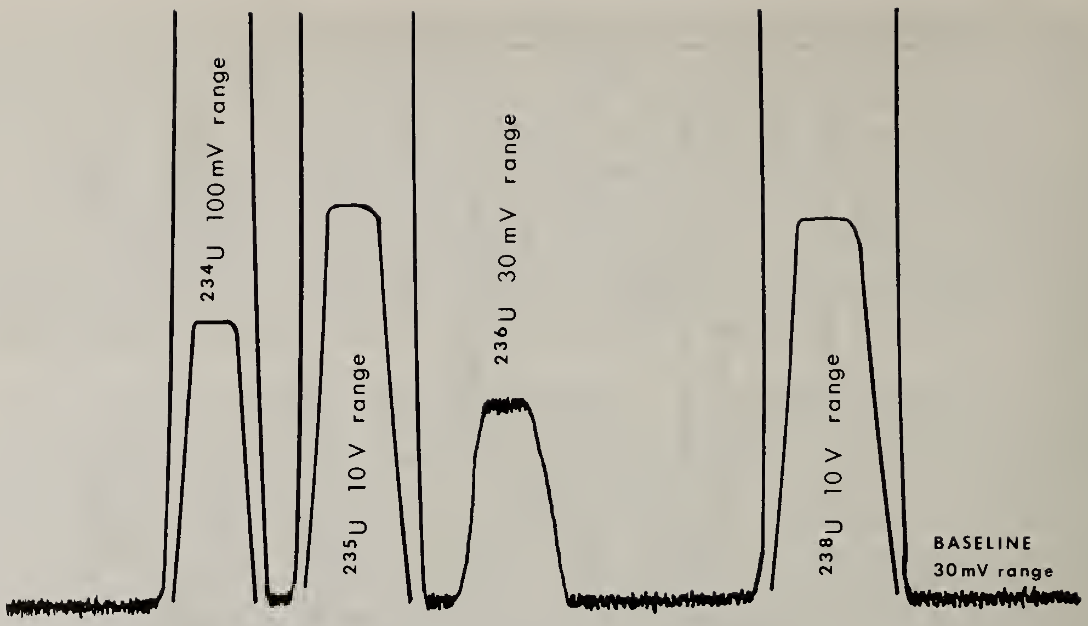

Figure 16. A typical mass spectral scan for uranium.

25. Standard Reference Materials

The analysis and certification of Standard Reference Materials (SRM's) has continued to be a major part of the total scientific effort of this Division. Input from virtually the entire scientific staff goes into this effort which accounts for about 25 percent of the total working budget. The Division funding 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 STRS portion of the funding is intended for the preliminary research necessary to develop the methodologies required for the actual production of SRM's. This year seven different research projects were funded by the Office of Standard Reference Materials. Once a sufficient technological foundation has been established through STRS research, then the WCF funding becomes operative. The WCF projects are those which result in the actual production of a marketable standard. The SRM's on which work was carried out this year and the STRS research projects, along with the relative effort in staff-years, are shown in Tables 11 and 12. It is seen from these tables that the work on SRM's was carried out on a wide variety of matrices (aqueous, biological, fossil fuel, metals, etc.). The concentration levels certified on these materials ranged from ultra-trace to major. A number of items on the lists presented here are described in greater detail, as technical accomplishments, throughout the Annual Report.

One important accomplishment this year was the recertification of three widely used primary chemical Standard Reference Materials (TRIS, Benzoic Acid, and Potassium Dichromate). The widespread use of these standards is

Table 11. WCF Work Carried Out on Standard Reference Materials.
Division 551, FY 81

SRM Number	TITLE	Effort S/Y
923	TRIS	.2
909	Sodium in Serum	.1
691a	Reduced Iron Oxide	.6
930d	Glass Filters for Spectrophotometry	.4
136d	Potassium Dichromate	.4
978a	Silver Assay and Isotopic	.1
1645 and 1648	River Sediments & Urban Particulates	.9
931c	Liquid Absorbance Filters for Spectrophotometry	.4
994	Gallium Assay and Isotopic	.1
962a and 963a	Fission Track Glasses	.2
1284a, 1285a, 72g, 1225, 1226, 1173	Low Alloy Steels	.4
C1137 and C1137a	White Cast Irons	.2
350a	Benzoic Acid	.2
1221, 1227, 1228	Basic Steels	.4
494-500, 1251-1253, 393-400	Copper Benchmarks	.9
1646	Estuarine Sediment	.2
U-002, U-020, U-050, U-200, U-970, U-500, U-150	Nuclear SRM's	.1
1034 and 1035	Sulfur in Unalloyed Copper and Tin Bronze	.2
1815a, 1816a	Lead in Reference Fuel Standards	.1
864-867, 1244-1247	Inconels and Incalloys	.3
C1151-C1154, 1269, 1270, 1270a	Low Alloy Steels	.9
1223	Stainless Steel	.1
1641b and 1642b	Mercury in Water	.2
125b, 1134, 854, 1254	Calcium in Low Alloy Steels	.1
1620a, 1621a, 1622b, 1623b, 1632b, 1634a, 1635a	Sulfur in Fuel Oils and Coal	.5
1649	Washington Dust	.2
1572 and 1577	Bovine Liver and Citrus Leaves	.2
1084 and 1085	Wear Metals in Oil	.1
1261-1265a	Low Alloy Steels	.3
		9.0

Table 12. STRS Projects Currently Underway.
Division 551, FY 81

Task	Description	Effort S/Y
Sulfur Analysis	Complete development of IDMS procedure and develop Leco CS-46 and ion chromatography procedures for application to a number of SRM's	.6
DC Plasma Spectroscopy	Complete development of dc plasma spectrometry technique	.4
Iodine in Foods	Application of the techniques being developed for the measurement of iodine in existing natural matrix SRM's	.4
Tin and Vanadium in Biologicals	Development of certification procedures for tin and vanadium and their application to biological SRM's	.6
Metal-on-Quartz Filters	Resolve research problems required for full scale production	.5
Light Elements in Complex Matrices	Development of analytical methods for the determination of C, H, N, O, and S in matrices such as coal, oil, and plant tissue	.6
Copper Benchmarks	Complete technique development necessary for certification of Copper Benchmarks	.7
		3.8

best illustrated by the fact that nearly 500 units of the three materials are sold each year.

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 River Sediment, Estuarine Sediment, Urban Particulates, Washington Dust, Bovine Liver, Citrus Leaves, and Mercury in Water. Additionally, work has begun leading to the certification of a set of three coal samples and four fuel oil samples which will be certified for sulfur content and issued as SRM's.

Each year significant effort goes into the analysis of a large number and variety of metals. This work is done for acceptance testing, to determine homogeneity, and for eventual certification of both trace and major constituents. The Division effort in this area accounts for about 40 percent of the entire budget allotted for Standard Reference Materials.

B. I. Diamondstone

C. Outputs and Interactions
(Inorganic Analytical Research Division)

1. Publications

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Diamondstone, B. I., "NBS Standard Reference Materials for Improving the Accuracy of Priority Pollutant Analyses," Proc. of Fifth Seminar on Analytical Methods for Priority Pollutants, Hershey, PA, April 9-10, 1981, in press.

Diamondstone, B. I., Burke, R. W., and Garner, E. L., "An NBS Approach for Improving the Quality of Leach Measurements on Solid Wastes," Proc. of International Conference on Solid Wastes, Sludges and Residual Materials: Monitoring, Technology and Management," Rome, Italy, June 17-20, 1981, in press.

Greenberg, R. R. and Kingston H. M., "Simultaneous Determination of Twelve Trace Elements in Estuarine and Sea Water Using Pre-Irradiation Chromatography," J. Radioanal. Chem., in press.

Koch, W. F. and Stolz, J. W., "Analysis of Chloride-Doped Cadmium Sulfide by Ion Chromatography," Anal. Chem., in press.

Moore, L. J., Murphy, T. J., Barnes, I. L., and Paulsen, P. J., "Absolute Isotopic Abundance Ratios and Atomic Weight of a Reference Sample of Strontium," J. of Res. Nat. Bur. Stand., Jan.-Feb., 1982, in press.

Moody, J. R., "Sample Handling and Storage for Trace Analysis," Proc. of the Royal Society of Chemistry, Talanta, in press.

Moody, J. R., "Some Considerations of Analytical Methodology Relevant to Radioactive Solid Leachate Testing," Nuclear and Chemical Waste Management, in press.

Zeisler, R., "Trace Element Analysis," in Pilot Program for the National Environmental Speciman Bank - Phase I, p. 29, National Technical Information Service, Springfield, VA, in press.

Bower, V. E., Davis, R. S., Murphy, T. J., Paulsen, P. J., Gramlich, J. W., and Powell, L. J., "Recalculation of the Faraday Constant Due to a New Value for the Atomic Weight of Silver," to be published in J. of Res. Nat. Bur. Stand.

Harrison, S. H., Zeisler, R., Anderson, D. L., "Evaluation and Analysis of Environmental Specimen Bank Samples by Nuclear Methods," to be published in J. Radioanal. Chem.

Powell, L. J., Murphy, T. J., and Gramlich, J. W., "The Absolute Isotopic Abundance and Atomic Weight of a Reference Sample of Silver," to be published in J. of Res. Nat. Bur. Stand.

Zeisler, R. and Greenberg, R. R., "Ultratrace Determination of Platinum in Biological Materials Via Neutron Activation and Radiochemical Separation," to be published in J. Radioanal. Chem.

2. Talks

Rains, T. C. and Alvarez, R., "Characterization of Standard Reference Materials for Trace Metal Determination," 9th International Conference on Atomic Spectroscopy and XXII Colloquium Spectroscopicum Internationale, Tokyo, Japan, September 5, 1980.

Moody, J. R., "Sample Handling and Storage for Trace Analysis," Royal Society of Chemistry Meeting, Cardiff, England, September 23, 1980. Invited

Harrison, S. H., "The National Environment Specimen Bank Program at NBS," University of Maryland, Division of Nuclear and Environmental Chemistry, College Park, MD, September 26, 1980. Invited

Lutz, G. J., "Photon Activation Analysis - A Review," 7th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 30, 1980. Invited

Epstein, M. S. and Rook, F. L., "An Evaluation of Noise Sources which Limit Precision in the Optimum Analytical Range of Atomic Spectroscopic Methods," 7th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 30, 1980. Invited

Moody, J. R., "Clean Air Fume Hoods for Trace Element Analysis," Laboratory of the Government Chemist, London, England, October 1, 1980. Invited

Rains, T. C., "A Comparison of Electrothermal Atomization and Hydride Generation Atomic Absorption Spectrometry for As and Se," 7th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, October 3, 1980.

Rains, T. C., "A Method to Improve the Precision and Accuracy of Atomic Absorption Spectrometry with Electrothermal Atomization," 7th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, October 3, 1980.

Fassett, J. D., Kelly, W. R., and Machlan, L. A., "Mass Spectrometric Analysis of Nanogram Levels of Plutonium," 24th Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 7, 1980. Invited

Powell, L. J., "Career Opportunities in Science for the 80's," North Dakota State University, Fargo, ND, October 25, 1980. Invited

Epstein, M. S., "Review of Analytical Methods for Liquids and Solutions at NBS," Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials, Battelle Pacific Northwest Labs, Richland, WA, November 11, 1980.

Lutz, G. J., "Analytical Method Review - Activation Analysis of Solids," Workshop on Compositional and Microstructural Analysis of Nuclear Materials, Battelle Pacific Northwest Labs, Richland, WA, November 11, 1980. Invited

Epstein, M. S., "Some Developments in Atomic Absorption and Emission Spectroscopy at the National Bureau of Standards," Cincinnati Section, Society for Applied Spectroscopy, Cincinnati, OH, November 13, 1980. Invited

Zeisler, R., "Phase I of the National Environmental Specimen Bank Pilot Program at the National Bureau of Standards," Medical Science Colloquium, University of Minnesota, Minneapolis, MN, December 1, 1980. Invited

Norris, J. A., "Splitting Hairs," New England Section, Society for Applied Spectroscopy, Waltham, MA, December 4, 1980. Invited

Moody, J. R., "Some Considerations of Analytical Methodology Relevant to Radioactive Solid Leachate Testing," Oak Ridge Conference on the Leachability of Radioactive Solids, Gatlinburg, TN, December 9, 1980. Invited

Rains, T. C., "Analysis of Trace Metals in Water by Atomic Absorption Spectrometry," 1980 American Water Works Quality Technology Conference, Miami Beach, FL, December 9, 1980. Invited

Diamondstone, B. I., "Extraction Procedures for Solid Wastes," 2nd Annual Midwest Conference on Environmental Laboratory Technology, St. Paul, MN, December 10, 1980. Invited

Kingston, H. M., "State-of-the-Art Analytical Measurements of Trace Elements in Aqueous and Other Matrices with an Emphasis on Chemical Manipulation," Rockwell International Labs, Richland, WA, January 27, 1981. Invited

Kingston, H. M., "Trace Metal Analysis: The Effect of Chemical Manipulation on the Results," Battelle Pacific Northwest Labs, Richland, WA, January 28, 1981. Invited

Lutz, G. J., "Photon Activation Analysis," Analytical Nuclear and Environmental Chemistry Division, University of Maryland, College Park, MD, January 30, 1981. Invited

Greenberg, R. R., "Neutron Activation of Estuarine Water and Suspended Solids," Analytical Nuclear and Environmental Chemistry Division Seminar, University of Maryland, College Park, MD, February 6, 1981. Invited

Powell, L. J., "Careers in Chemistry," Seneca Valley High School, Gaithersburg, MD, February 10, 1981. Invited

Koch, W. F., "Anion Analysis by Ion Chromatography at the National Bureau of Standards," Joint Meeting of the Chemical Society of Washington and the Electrochemical Society, Montgomery College, Rockville, MD, February 12, 1981. Invited

Powell, L. J., "Careers in Chemistry," Gaithersburg High School, Gaithersburg, MD, March 3, 1981. Invited

Epstein, M. S. and Rains, T. C., "Atomic Absorption Spectrometry," ACS Short Course, Pittsburgh Conference, Atlantic City, NJ, March 8, 1981.

Moore, L. J., "Some New Approaches to Ion Production and Measurement," Chemical Physics Laboratory, National Institutes of Health, Bethesda, MD, March 19, 1981. Invited

Rains, T. C., "Modern AAS Techniques - Characterization of NBS Standard Reference Materials," National Society for Applied Spectroscopy Tour Speaker, Lehigh Valley Section, Reading, PA, April 6; Delaware Valley Section, Philadelphia, PA, April 7; New York Section, New York, NY, April 8; and New England Section, Boston, MA, April 9, 1981. Invited

Diamondstone, B. I., "NBS Standard Reference Materials for Improving the Accuracy of Priority Pollutant Analyses," 5th Seminar on Analytical Methods for Priority Pollutants, EPA, Hershey, PA, April 10, 1981. Invited

Norris, J. A., "Metal Homogeneity," Lehigh Valley Section, Society for Applied Spectroscopy, Reading, PA, April 24, 1981. Invited

Powell, L. J., "A New Determination of the Atomic Weight of Silver and an Improved Value for the Faraday," Mass Spectrometry Discussion Group of Washington, Washington, DC, May 18, 1981. Invited

Greenberg, R. R., Kingston, H. M., and Beary, E. S., "Non-Normal Distribution of Blanks in Environmental Samples," 11th Annual Symposium on the Analytical Chemistry of Pollutants, Jekyll Island, GA, May 18, 1981. Invited

Wise, S. A. and Zeisler, R., "Analytical Methods for Certification of Standard Reference Materials," Chemistry Colloquium, Institut fur Oekologische Chemie, GSF, and Institut fur Chemie, TU München, Weihenstephan, F.R. Germany, May 18, 1981. Invited

Harrison, S. H., "Implementation and Evaluation of Sample Collection for Human Livers," Environmental Specimen Banking Project - Seminar of State and Planning 1981, Kernforschungsanlage (KFA), Jülich, F.R.G., May 20, 1981. Invited

Harrison, S. H. and Zeisler, R., "Development and Evaluation of Cryogenic Homogenization of Tissue," Environmental Specimen Banking Project - Seminar of State and Planning 1981, Kernforschungsanlage (KFA), Jülich, F.R.G, May 20, 1981. Invited

Zeisler, R. and Harrison, S. H., "Specimen Storage and Storage Evaluation," Annual Bilateral Meeting on Specimen Banking by US/EPA and Ummeltbundesant, F.R.G., Jülich, F.R.G., May 20, 1981. Invited

Zeisler, R., "Inorganic Analysis of Liver Specimens Collected During the First Year of the NESB Pilot Program," Annual Bilateral Meeting on Specimen Banking by US/EPA and Ummeltbundesant, F.R.G., Jülich, F.R.G., May 20, 1981. Invited

Paulsen, P. J. and Burke, R. W., "Isotope Dilution Spark Source Mass Spectrometry - Determination of Sulfur in NBS Iron Base Alloys," 29th Annual Conference of the American Society for Mass Spectrometry, Minneapolis, MN, May 24, 1981. Invited

Kelly, W. R. and Fassett, J. D., "The Determination of Subnanogram Quantities of Uranium by Isotope Dilution Mass Spectrometry," 29th Annual Conference on Mass Spectrometry and Applied Topics, Minneapolis, MN, May 27, 1981. Invited

Kingston, H. M., "Workshops on Spiking Procedures for Isotope Dilution Mass Spectrometry," 29th Annual Conference of the American Society for Mass Spectrometry, Minneapolis, MN, May 27, 1981. Invited

Epstein, M. S. and Rains, T. C., "Atomic Absorption Spectrometry," ACS Short Course, National Bureau of Standards, Washington, DC, June 5, 1981.

Powell, L. J., "A New Determination of the Atomic Weight of Silver and an Improved Value for the Faraday," 2nd International Conference on Precision Measurements and Fundmental Constants, National Bureau of Standards, Washington, DC, June 10, 1981. Invited

Garner, E. L., "An NBS Approach for Improving the Quality of Leach Measurements on Solid Wastes," International Conference on Solid Wastes, Sludges, and Residual Materials: Monitoring, Technology, and Management, Rome, Italy, June 17, 1981. Invited

Greenberg, R. R. and Kingston, H. M., "Simultaneous Determination of Twelve Trace Elements in Estuarine and Seawater Using Pre-Irradiation Chromatography," 6th International Conference on Modern Trends in Activation Analysis, Toronto, Canada, June 18, 1981. Invited

Zeisler, R. and Greenberg, R. R., "Ultratrace Determination of Platinum in Biological Materials via Neutron Activation and Radiochemical Separation," 6th International Conference on Modern Trends in Activation Analysis, Toronto, Canada, June 18, 1981.

Moore, L. J., "Application of Thermal Ionization to Stable Isotopic Trace Measurements," Workshop on Stable Isotopic Measurements on Metals, Children's Nutrition Research Center, Baylor College of Medicine, Houston, TX, June 22, 1981. Invited

Fleming, R. F., "Analytical Chemistry at the NBS Reactor," Analytical Chemistry Division Seminar, Oak Ridge National Laboratory, Oak Ridge, TN, July 17, 1981. Invited

Koch, W. F., "Anion Analysis by Ion Chromatography at the National Bureau of Standards," International Symposium on Ion Chromatography, 23rd Rocky Mountain Conference, Denver, CO, August 3, 1981. Invited

Rains, T. C., "Atomic Absorption Spectrometry," ACS Short Course, 23rd Rocky Mountain Conference, Denver, CO, August 6, 1981.

Fassett, J. D., Moore, L. J., and Travis, J. C., "Innovations in High Sensitivity Mass Spectrometry," Gordon Research Conference, New Hampton, NH, August 12, 1981. Invited

Rains, T. C. and Messman, J. D., "Application of Liquid Chromatograph - Atomic Absorption Spectrometry for Determining Metal Species in Environmental Samples," 9th International Conference on Atomic Spectroscopy and XXII Colloquium Spectroscopicum Internationale, Tokyo, Japan, September 4, 1981.

Rains, T. C., "Critical Evaluation of the Determination of Arsenic and Selenium by Atomic Absorption Spectrometry," 9th International Conference on Atomic Spectroscopy and XXII Colloquium Spectroscopicum Internationale, Tokyo, Japan, September 8, 1981. Invited

Rains, T. C., "Sampling, Preservation, and Standardization in Trace Metal Analysis," Seoul International Spectroscopy Conference, Seoul, Korea, September 11, 1981.

Moore, L. J. and Travis, J. C., "Laser-Induced Ion Fluorescence in Magnetic Sector Mass Spectrometry," 8th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 22, 1981.

Watters, R. L., Jr., "Analytical Techniques Using the Inductively Coupled Plasma," FACSS Workshop, 8th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia Sheraton, Philadelphia, PA, September 22, 1981. Invited

Epstein, M. S. and Blundell, C. G., "Analysis of Nuclear Waste Leachates for Trace Elements by Atomic Spectrometry: Problems and Solutions," 8th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 23, 1981. Invited

Epstein, M. S. and Blundell, C. G., "Considerations for Obtaining the Utmost in Accuracy Using D.C. Plasma," 8th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 23, 1981. Invited

Kingston, H. M., "The Analytical Constraints That Influence Leachability Measurements and Reference Materials" 8th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 23, 1981. Invited

Rains, T. C. and Powell, L. J., "The Art of Sample Preparation," FACSS Short Course, 8th Annual Meeting of the Federation for Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 24, 1981. Invited

Zeisler, R., "Pilot Environmental Specimen Bank - The Analytical Approach," Environmental Pathology Seminar, Harbor Grace Medical Center, Seattle, WA, September 28, 1981. 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-19.07.04, Section on Chemical Characterization of Fluvial Sediment
    - ASTM D-19, Water
- Chairman, Fellowship Award Committee, Baltimore-Washington Section of the Society for Applied Spectroscopy
- Secretary/Treasurer, Baltimore-Washington Section of the Society for Applied Spectroscopy
- Delegate, FACSS Governing Board for the Division of Analytical Chemistry of the American Chemical Society
- Budget Committee Member, FACSS Governing Board

Ronald F. Fleming
- Member, Organizing Committee, Fifth Symposium on X- and Gamma-Ray Sources and Applications
    - Organization and Planning Committee, The Fourth International Conference on Neutron Transmutation Doping of Semiconductors
    - Committee on Accelerator-Based Neutron Research at NBS

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

William R. Kelly
- Member, Center Colloquium Committee

Howard M. Kingston
    Member, NBS Nuclear Waste Management Team

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

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

E. June Maienthal
    Member, ASTM D-19, Water
        ASTM D-19.05, Inorganic Constituents in Water
        ASTM D-19.06, Methods for Analysis for Organic Substances in Water
        ASTM D-19.07, Methods of Testing of Water-Reformed Deposits and Properties of Water
        ASTM D-19.07.04.03, Trace Metals and Sediments
        ASTM D-19.11, Methods for the Analysis of Water for Power Generation and Process Uses
        ASTM E-3, Metals
        ASTM E-3.01, Ferrous Metals
        ASTM E-3.02, General Analytical Practices
        ASTM E-3.05, Non-Ferrous Metals

George Marinenko
    Member, ASTM D-19, Water
        ASTM D-19.01, Saline in Brackish Waters
        ASTM D-19.02, General Specifications and Technical Resources
        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-19.02.02.01, Interpretation of Results
    Vice-Chairman, National Capital Section of the Electrochemical Society
    Program Chairman, National Capital Section of the Electrochemical Society

John R. Moody
    Member, ASTM D-19, Water
        ASTM D-19.05, Inorganic Constituents in Water
        Audit Committee, Chemical Society of Washington
    Delegate, Middle Atlantic Regional Meeting, Chemical Society of Washington

Larry J. Moore
    Contributing Editor, Journal of Applied Spectroscopy

Thomas J. Murphy
- Member, American Chemical Society Committee on Analytical Reagents
  - American Chemical Society Committee on Membership Affairs
  - American Chemical Society Admissions Committee
  - 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, 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
  - Investment Committee, Chemical Society of Washington
  - Board of Managers, Chemical Society of Washington
- Chairman, Committee on Isotope Ratio Measurements, American Society for Mass Spectrometry
  - Budget Committee, Chemical Society of Washington
- Treasurer, 15th Middle Atlantic Regional Conference, American Chemical Society
- Assistant Registration Chairman, Federation of Analytical Chemistry and Spectroscopy Societies

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-Elect, 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

Robert L. Watters, Jr.
Secretary, ICP Detection Limits Committee
National Correspondent and Reviewer Designate, ICP Information Newsletter

4. Other

a. Seminars

October 7, 1980 - Kenneth Grabowski, Argonne National Laboratories, Argonne, IL, "Compositional Mapping Using MeV Ion Beams"

December 1, 1980 - John A. Norris, Atomic & Molecular Spectrometry Group, Inorganic Analytical Research Division, National Bureau of Standards, Washington, DC, "Mini-inhomogeneity in Ferrous Standard Reference Materials"

December 11, 1980 - Sharon M. Tomaski, Department of Chemistry, Rutgers University Camden, NJ, "Collection and Treatment of Hair Samples for Elemental Analysis"

March 13, 1981 - Rebecca Koszykowski, Lawrence Livermore Laboratory, Livermore, CA, "Analysis of Solar Grade Silicon by Neutron Activation and ICP-OES"

July 1, 1981 - Paul DeBievre, Central Bureau for Nuclear Measurements, Geel, Belgium, "A Determination of the ^{241}Pu Half-Life of 90% Enriched Material"

July 27, 1981 - Jan Lindberg and Mats Lindgren, Analytical Research, Pharmacia AB, Uppsala, Sweden, "Some Applications of IC and ICE in the Pharmaceutical Industry" and "Investigation of the Determination of SO_3^{2-} with IC"

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 (an area in which we foresee increasing need for accurate analytical chemistry and Standard Reference Materials). Results of Division research are utilized by other Federal agencies, industry, public and private institutions, and research programs at the National Bureau of Standards.

Substantial progress has been made in research on basic techniques in organic analytical chemistry and in furthering our understanding of measurement principles in this area. The Division is now actively involved in two competence building programs, selected for funding by the NBS Director. Results of our research in these two areas, Organic Electrochemistry and the Analysis of Ionization Mechanisms and Ion Structures, as well as highlights of other technical accomplishments during the past year, are contained in the group overviews and individual technical highlights which follow.

A major achievement of the past year was completion of an international collaborative study between NBS and the Karolinska Institute in Stockholm, Sweden, which resulted in the first successful intercomparison of definitive clinical chemical methodology. Results of the study indicate good agreement between NBS and Swedish isotope dilution mass spectrometric measurements of serum cholesterol. Research in two-dimensional NMR spectroscopy was extended to the total analysis of the proton NMR spectra of α- and β-$\underline{D}$-glucose, the principal constituents of SRM $\underline{D}$-glucose. Two-dimensional proton NMR has also been applied to several additional molecules including digoxin, which is being evaluated as a candidate SRM and for which a definitive method for its determination in serum will be pursued. A new interface has been designed and installed to permit capillary column gas chromatographic operation of our Fourier transform infrared (FT-IR) spectrometer with simultaneous acquisition of a flame ionization detector signal. In response to EPA needs in the development of a Master Analytical Scheme for organic pollutants in water, NBS has supplied "marker compound" solutions to be used in evaluating the quantitative accuracy and viability of the scheme. In the organic electrochemistry program, research has been initiated on chemically modified electrodes and a mathematical model has been developed for electron transfer processes in molecules with interactive multiple redox centers. We have also begun some exciting research on the use of on-line multidimensional liquid chromatography for the quantitation of individual analytes in complex samples.

Research on a number of challenging SRM's has been completed or is nearing completion. Amongst these SRM's are air particulate matter certified for polynuclear aromatic hydrocarbons, a polychlorinated biphenyl (PCB) in transformer and lubricating oil, a purified decapeptide (angiotensin), and a human serum certified for the two most recently approved anticonvulsant drugs, valproic acid and carbamazepine.

As in past years, the Division continued to perform service analyses for other groups. Analyses have included samples for the FDA relating to the determination of the cause of Toxic Shock Syndrome, calibration of the optical rotation of quartz control plates for the sugar industry, and identification of oxidation products of polystyrene for the Polymers Division at NBS. Recently, we have been fortunate to have two people on sabbatical leave from universities temporarily join our staff through the Intergovernmental Personnel Act. They are working on problems relating to the pilot National Environmental Specimen Bank and the development of selective detection techniques in chromatography.

In the coming year we hope to initiate a new program in bioanalytical technology. A presentation on Proteins in Analytical Chemistry was recently given to the NBS Director as one of this year's competence building proposals. We believe that a major key to the future in sensitive, selective and precise quantitation in complex samples will be through the use of proteins as analytical reagents. We look forward to initiating research in this area.

With the arrival of an advanced pulse programmer, currently on order, we plan on extending our NMR research efforts to include heteronuclear two-dimensional NMR and sensitivity enhancement by cross polarization techniques. We plan on extending our research effort in GC/FT-IR spectroscopy to isotope dilution GC/FT-IR for the quantitative analysis of trace constituents in complex samples. The competence building program on the analysis of ion structures will be directed toward the investigation of collisional activation and laser induced metastable ion generation for the analysis of large organic molecules. In the competence building program in organic electrochemistry, research on chemically modified electrodes will be expanded and recently developed mathematical models will be used in understanding the redox phenomena which occur at polymer modified electrodes. Our research efforts in on-line multidimensional LC will be expanded to the more difficult task of quantitating polar compounds in complex samples.

Major programmatic thrusts during the next few years are seen in two areas. The first, already briefly mentioned, is food and nutrition; we see an increasing need for accurate analysis of organic nutrients, as well as food contaminants and natural toxins. The proceedings of a workshop held at the Bureau to discuss Reference Materials for Organic Nutrient Measurements have been compiled and recommendations have been made for the currently most useful and technically feasible SRM's for water-soluble and fat-soluble vitamins. The second area of major impact will be the analysis of organic constituents in hazardous wastes. Current indications are that a firm scientific basis will be required for the promulgation of further regulations in this area. This will put a heavy burden on developing accurate methods and reference materials for the analysis of these wastes. In addition to our initial research in this area, we recently have been called upon to provide a critical, peer review of the EPA-sponsored analyses of samples from the Love Canal area.

In summary, the future shows many promising areas of research in organic analytical chemistry and no shortage of problems for the application of research results.

1. Bioanalytical Group: Overview

The mission of the Bioanalytical Group is to enhance the accuracy of measurement of simple-to-macromolecule organic compounds of widespread bioanalytical importance, through research employing enzymologic, electrophoretic, immunologic, radiochemical, spectrophotometric, and thin layer chromatographic techniques.

A major thrust during the past year has been the continued development of definitive methods for organic analytes in serum. The candidate definitive method for uric acid is complete and a manuscript is in preparation. The accuracy of the NBS candidate, definitive isotope dilution/mass spectrometry (ID/MS) method for total serum cholesterol has been compared with the ID/MS method developed at the Karolinska Institute (KI) which KI uses as a reference method. The initial interlaboratory comparison of five serum pools revealed a bias between the two methods: all the mean values ($n = 8$) obtained at the KI were lower than the NBS means, the average difference was -1.3 percent. NBS traced the source of bias to the impure cholesterol KI used as primary standard. With NBS SRM cholesterol used at the KI and new analyses for comparison, the bias was removed. The average difference in means was +0.2 percent, which was not significant since the new KI mean values differed as much as ±1.5 percent from the NBS values. In both comparisons, the standard deviations of the NBS results were several-fold smaller than the KI's. The intercomparison is described in a joint paper submitted to *Clinical Chemistry*.

Multilaboratory test data have been gathered for evaluating the American Association for Clinical Chemistry's (AACC) hexokinase/glucose-6-phosphate dehydrogenase candidate reference method for serum glucose. The Bureau's initially developed ID/MS method for glucose involving diacetone glucose (DAG), was used for determining the target values for the serum pools employed in the evaluation of the candidate reference method. The evaluation and the ID/MS method are now the subjects of a manuscript undergoing NBS review. Publication was withheld because after these studies were initially thought to be complete subsequent analyses by both methods revealed different and unexpected results. These are now known to be due to changes in serum glucose levels that occurred during storage at -20 °C.

At the current time, and in FY 1982, research continues on the development of definitive ID/MS methods for creatinine and urea. In 1982, it is anticipated that research will begin on triglyceride and digoxin definitive methods.

We have participated in the development of a reference method for total serum protein in cooperation with the Standards Committee of the AACC. NBS SRM 927, Standardized Protein Solution, is used for calibrating the method.

Schaffer and Reeder are co-authors in the two papers on this subject, published in Clinical Chemistry.

Following a protocol devised by Dr. Robert McComb at Hartford Hospital, our Group participated in a round robin with four other laboratories performing accurate measurement of lactate dehydrogenase activity in lyophilized human serum. It was necessary to know the reaction temperature within 0.1 °C, with the further requirement that the reaction be run within 0.3 °C of 29.77 °C, the gallium melting point. For the most recent round robin, the activity found was 233.7 U/L with a relative standard deviation of 4.99 percent.

For an FDA-sponsored study on the identification and physiological effect of leachable materials from polymeric implants used for human patients, we developed a reliable assay for prolyl hydroxylase activity, using highly labeled substrate and active enzyme, both prepared in our laboratory. The enzyme is involved in the formation of collagen which is believed to be a cause for the failure of silicone polymer breast implants; it has been postulated that the leachable compounds enhance enzyme activity.

In continuing research on the extension of immunoassay procedures to the analysis of industrial effluents, considerable effort has gone into the organic synthesis of a tracer compound that has both a fluorescent moiety and a dinitrophenol structure. Pilot batches of such a tracer were prepared by reacting fluoresceinamine (Isomer I) and 2,4-dinitrobenzene sulfonylchloride. Although the compound is still not pure, there is good evidence that this synthetic procedure produces sufficiently active tracer to make it useful in an immunoassay. Work has also been focused on the selection and purification of specific antibodies by means of affinity column purification methods. In the near future, we will be directing our efforts toward developing other solid-phase reagents, and increasing the reproducibility and sensitivity of the immunoassay system.

In conjunction with the Electrochemistry Group, we found evidence for the chemical equivalency of carbonyl oxygen and dicyanomethylene groups in a series of croconate salts, and have proposed a mechanism for the superconductivity of potassium croconate violet. Three papers on these subjects are in preparation.

Finally, during the past year, we presented a competence proposal on Proteins in Analytical Chemistry to the Director of NBS. This area of research, we believe, will play a major role in the future of analytical chemistry and we anxiously look forward to our expanded involvement. Initial efforts will be directed toward utilization and standardization of two-dimensional electrophoresis.

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

2. Electrochemistry Group: Overview

The competence building program in organic electrochemistry has made good progress in the chosen research directions and we have begun applying this research to NBS programmatic areas. During the third 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 other research areas.

In the area of spectroelectrochemistry, the setting up and evaluation of vidicon and diode array detectors for the optical multichannel analyzer has been completed. Using an optically transparent thin-layer cell with a gold minigrid working electrode, the spectroelectrochemical behavior of the very complex blue copper protein, ceruloplasmin, is being investigated. Since metalloenzymes of this type normally undergo irreversible heterogeneous electron transfer, the first part of this research project involves the study of redox mediators which facilitate electron transfer. Initially, these are being studied as homogeneous electron transfer mediators, but they may eventually be bound to the metallic electrode substrate to function as chemically modified electrodes which will catalyze these redox reactions at the electrode surface directly. Spectroelectrochemical studies have also been performed on croconate salts (which are excellent model compounds because the intense coloration of croconate solutions can be reversibly altered by electrochemical means) and also interesting chemicals as a consequence of their semiconductor behavior and potential use as electrochromic display materials. As part of this research, a special multipurpose cell was designed for performing spectroelectrochemical studies and other types of aqueous and nonaqueous electrochemistry.

Surface-enhanced Raman spectroscopy has been the most recent project initiated in the area of spectroelectrochemistry. While the initial research has been concerned with the study of the interactions of pyridine derivatives with silver and mercury electrodes, it is expected that this technique will prove to be extremely useful in studying the orientation and conformation of molecules bound to electrodes in our chemically modified electrode research. In addition, it is expected that these studies will help to explain the surface-enhancement phenomenon for which no accepted theory exists.

The development of electrochemical detectors for liquid chromatography has continued with the use of dual-electrode sensors and modulated excitation waveforms to achieve maximum selectivity and sensitivity for a variety of important analytes. This technique is being applied to the determination of organomercury species in fish tissue and the pilot National Environmental Specimen Bank samples. In addition to the development of the electrochemical detectors themselves, considerable effort is being applied to the elucidation of the electrochemical processes occurring at the generator and detector electrodes and to the sample extraction techniques that are required to maintain the integrity of the analyte species.

The research project on chemically modified electrodes is being applied to the development of an amperometric sensor for halogenated hydrocarbons such as polychlorinated biphenyls and organochlorine pesticides. The proposed sensor will electrocatalytically reduce these types of compounds via nickel Schiff-base complexes which act as redox centers and are attached to the metallic electrode by means of polyphenylene oxide films. An alternate approach will employ a polyvinylferrocene polymer attached to the electrode substrate. It is planned to use these electrodes directly as selective and sensitive sensors and also as detectors in chromatographic systems.

In response to needs in several Division programs, research is continuing on a photoelectrochemical sensor for carboxylic acids. This device is based on a semiconductor electrode, n-type TiO_2, which, when irradiated by UV light, causes the oxidation of carboxylic acids at very low applied potentials. Since the oxidation of water interferes with the direct determination of the carboxylic acids, an indirect approach monitoring the carbon dioxide produced in the photo-Kolbe reaction has been employed. Initial experiments using a gas-permeable membrane and differential conductance measurements have demonstrated the feasibility of this approach, but response was too slow for practical use. Work is continuing using a carbon dioxide electrode in an attempt to increase the response time of this system.

Redox process modeling and digital simulation have been used to develop models to obtain thermodynamic and kinetic reaction parameters. An example of this work was the derivation of a mathematical model for electron transfer in molecules with interacting multiple redox centers. It is expected that these models will be useful in explaining the redox phenomena that occur at polymer modified electrodes. More recently, theories and simulations have been developed to describe the current-time behavior in chronoamperometry employing unshielded disk electrodes and in determining diffusion coefficients from such experiments.

Our plans for the coming year call for continued research on the above projects with expanded efforts in the area of chemical modification of electrodes as selective organic sensors. These basic studies are expected to be rapidly adapted to address the analytical needs of the Center.

Richard A. Durst, Group Leader; Elmo A. Blubaugh, Kathryn A. Bunding, Lawrence M. Doane, Mary Lou Fultz, William A. MacCrehan, William T. Yap

3. Gas Chromatography Group: Overview

During FY 1981 the Gas Chromatography (GC) Group has pursued basic analytical research in the design and implementation of an advanced GC Fourier Transform Infrared (FT-IR) interface. The interface now contains a Nicolet experimental low dead volume light pipe which improves spectral sensitivity and a flame ionization detector (FID) which allows simultaneous FID/FT-IR detection. A spectral library containing over 60 vapor phase IR spectra of polychlorinated biphenyl isomers has been constructed and will be used for PCB isomer identification and quantitation on real-world samples. The Group also demonstrated that it is feasible to perform isotope dilution gas chromatographic (ID/GC) analyses using FT-IR detection and in FY 1982 plans on developing a method for ID/GC/FT-IR quantitation using polynuclear aromatic hydrocarbons (PAH) in environmental samples. Additionally, a large amount of software has been written in the last year in support of our GC/FT-IR research. In the last year, we have prepared mixed liquid crystal-silicone polymer stationary phase wall-coated open tubular (WCOT) columns and have shown that these columns yield superior separations of PAH over conventional silicone phase WCOT columns. Software has been written for the determination of the correlation between molecular structure and chromatographic retention, and additional routines have been written for general data reduction.

The group has been actively involved in the Standard Reference Material program. We have participated in the certification of five new SRM's:

1. Polynuclear Aromatic Hydrocarbons in Acetonitrile, SRM 1647
2. Polychlorinated Biphenyls in Oil, SRM 1581
3. n-Heptane (Engine Octane Number Standard), SRM 1815a
4. Polynuclear Aromatic Hydrocarbons on Air Particulate Matter, SRM 1649
5. Valproic Acid and Carbamazepine in Human Serum, SRM 1599

The certification of the PAH SRM's required the use of newly implemented state-of-the-art on-column injection techniques. The Group has also completed a study of the feasibility of the preparation and certification of a halocarbons in drinking water SRM and will begin certification measurements in FY 1982.

During FY 1981 we have performed numerous service analyses and conducted several studies for other agencies. We prepared, analyzed, and determined the short range stability of a solution of organic compounds in hexane to be used by EPA for calibration of its Level I analysis method. The solution contained nine compounds of varying chemical polarity ranging from dodecane (nonpolar) to benzoic acid (very polar), with specific compounds falling into the various column chromatographic fractions of EPA's Level I method.

The stability of marker compound solutions for EPA's Master Analytical Scheme was monitored by GC analysis. (More details of this collaborative project are contained in the Mass Spectrometry Group Overview.) In addition, analyses were performed for the pilot National Environmental Specimen Bank, human polymeric implant leachables program, the NBS recycled oil program, a Department of Energy analytical quality assurance program, and a Department of Energy program to identify compounds in aqueous leachates from hazardous wastes.

During FY 1982 the Group will continue its research into multidimensional chromatography and will apply this technique to the separation and quantitation of nitrogen-, sulfur-, and perhaps oxygen-heteroaromatic compounds found on particulate matter. Research on selective detection will also be continued using the existing FT-IR, conductivity, nitrogen, electron capture detectors, and a new sulfur/phosphorus photometric detector requested in our equipment planning.

Stephen N. Chesler, Group Leader; Sharon L. Bowie; Delmo Enagonio,
Franklin R. Guenther, Reenie M. Parris

4. Liquid Chromatography Group: Overview

The major emphasis of the research in the Liquid Chromatography Group continues to be focused on the development of high-performance liquid chromatographic methods for the analysis of individual compounds in complex mixtures. The applications of our research continue to be concentrated in the environmental and biomedical areas, although we have, during the past year, begun to address separation problems in the food and nutritional area, also.

Specific research accomplishments for the past year include: (1) Development of a relationship between polynuclear aromatic hydrocarbon (PAH) retention in reversed-phase HPLC and PAH partition behavior in a n-heptadecane (C-17)/acetonitrile/water model system. We found the solvent effects between the C-17 partition model and reversed-phase C-18 columns to be equivalent, indicating that differences in selectivity among C-18 columns are due to innate differences in the stationary phase and not to "salting out" effects from the mobile phase as proposed by Locke [1]. (2) Development of an on-line multidimensional system for the analysis of PAH in complex samples. This system features the on-line coupling of normal- and reversed-phase chromatographic systems using column affinity sequencing. (3) Continued development and use of our gas saturation-HPLC method for measuring ambient temperature vapor pressures of non-volatile compounds. This procedure is an extension of our dynamic coupled-column liquid chromatographic procedure for determining aqueous solubilities of PAH. Saturated vapor streams are generated by passing dry nitrogen through a column packed with analyte-coated sand. The analyte is extracted from the stream cryogenically either on a coil, or on a C-18 adsorption trap prior to quantitation by HPLC. We have been able to measure vapor pressures down to 10^{-4} Pa using this technique. (4) Development of a sequential HPLC-fluorometric method for determining amino-PAH in complex mixtures. Amino-PAH are isolated from the matrix using chromatography on an aminosilane (NH_2) column with a hexane/methylene chloride mobile phase. Quantitation is performed on an octadecylsilane column using an acetonitrile/water mobile phase and spectrofluorometric detection. This technique has been used to determine naphthylamines and aminoanthracenes in shale oil, coal liquids, and petroleum products. (5) Development of a Soxhlet extraction, nitromethane partition, HPLC-fluorometric procedure for quantifying selected

PAH on air particulate matter. (6) Initiation of a study of the retention characteristics of aza-arenes and sulfur aromatics on C-18 and NH_2 columns.

The LC Group has actively participated in the NBS Standard Reference Material (SRM) programs. During the past year, work on three SRM's has been completed. In SRM 1647, PAH in Acetonitrile, we determined the concentrations of the sixteen PAH on the EPA Priority Pollutant List. This SRM will be used as a calibrant in the liquid and gas chromatographic analysis of PAH. In SRM 1599, Anticonvulsant Drugs in Serum, we determined carbamazepine and valproic acid in a lyophilized human serum matrix. This SRM will be used as a quality control standard by clinical laboratories doing such assays. In SRM 910, Sodium Pyruvate, we have completed certification with comparative NMR and HPLC determinations of the concentration of pyruvate dimer. Sodium pyruvate is used as a substrate for measurement of the enzyme, lactic acid dehydrogenase.

Several other SRM certification activities are currently in progress. HPLC procedures are being used for purity determination of angiotensin, determination of ten polynuclear aromatic hydrocarbons on an air particulate sample, and certification of an indeno(1,2,3-cd)pyrene generator column.

During the past summer, the Group has acquired the services of Dr. Freeman Allen, Pomona College, Claremont, CA, and Dr. Cora Vogt, University of Missouri Trace Analysis Group, Columbia, MO. Both are spending one-year tours of duty at NBS as part of the Intergovernmental Personnel Act program.

In FY 1982, we plan to continue our program in reversed-phase retention mechanisms. Emphasis will be placed on investigating the effects of surface coverage and bonding type (monomer or polymeric) on chromatographic selectivity. A large portion of our research time will continue to be devoted toward developing selective detection procedures for HPLC effluents. In this regard, we plan to explore the use of electrochemical techniques for selective detection of nitroaromatics, evaluate an in-house constructed light pipe as a tool for improving sensitivity in LC/Fourier transform infrared spectroscopy, and evaluate an in-house constructed ultrasonic probe as a tool to allow us to perform quantitative reversed-phase LC/mass spectrometry.

We plan to further develop our on-line multidimensional HPLC system and investigate the feasibility of determining more polar compounds (i.e., aza-arenes, amino-PAH, phenols) using this approach. Finally, as a continuing effort in our food and nutrition research program, we plan to further investigate the chromatographic behavior of fat-soluble vitamins in an attempt to develop at least two independent analytical procedures for each of several vitamins.

Reference

[1] Locke, D. E. J. Chromatog. Sci., 12: 433; 1974.

Willie E. May, Group Leader; C. Freeman Allen, Jeanice M. Brown-Thomas, Richard G. Christensen, William F. Cuthrell, Walter F. Kline, Pamela J. Leech, Sam A. Margolis, William J. Sonnefeld, Cora R. Vogt, Patricia A. White, Stephen A. Wise

5. Mass Spectrometry Group: Overview

The major continuing efforts of the Mass Spectrometry Group have been directed to the development of mass spectrometric methods for the accurate quantitation of individual compounds in complex mixtures, the development of high-resolution mass spectrometric techniques for the analysis of high molecular weight compounds, and the development of a new liquid chromatography mass spectrometry (LC/MS) interface suitable for the analysis of analytes requiring reversed-phase LC. Other agency and programmatic research continues to be concentrated in the environmental and clinical areas. A major new effort which is part of the competence building program on "Analysis of Ionization Mechanisms and Ion Structures" began this year.

Isotope dilution definitive methods development for the quantitation of human serum constituents has continued in collaboration with the Bioanalytical Techniques Group. A human serum Standard Reference Material, SRM 909, was released in September, 1980 with certified values for glucose and uric acid. Cholesterol certification was completed this year. The results of a cooperative study with the Karolinska Institute comparing two isotope dilution/mass spectrometry (ID/MS) methods for cholesterol have been accepted for publication in *Clinical Chemistry* and a manuscript describing and comparing two ID/MS methods for glucose developed at NBS has been prepared. Method development is in progress for urea and creatinine in serum.

Further work has been done on the development of an LC/MS interface. The LC/MS interface employing continuous sample preconcentration which was developed during the last several years and an example of quantitation using the system has been published. A new design of the probe utilizing ultrasonic nebulization allows the use of aqueous mobile phases.

Two projects utilizing the high resolution mass spectrometry facility are presently producing interesting results. In one, a method to obtain complete high resolution field desorption spectra and accurate mass measurements using silver sulfonate salts for mass calibration and photoplate detection has been developed and tested on some peptides. The second project is part of the mass spectrometry competence building program, "Analysis of Ionization Mechanisms and Ion Structures," and involves laser induced metastable ion generation as a selective probe for molecular structure. The photodissociation of ions created by electron impact has been observed for a variety of molecules.

A survey of the literature and a limited series of GC/MS experiments have been performed to explore the potential of negative chemical ionization mass spectrometry for quantitation. The first compounds studied were several phenols and nitrogen-heterocycles. Neither gave better sensitivity than positive chemical ionization. The phenols, however, produced interesting and apparently unreported fragmentation which will be investigated further. Quantitative accuracy and precision will be explored for compounds with high electron affinities such as halogenated pesticides and polychlorinated biphenyls which are known to yield high sensitivities in the negative ion mode.

Methods have been investigated for the analysis of several aqueous effluents from coal gasification, oil shale retorting, and petroleum refining for selected phenolic and polynuclear aromatic hydrocarbon (PAH) species. A simple extraction procedure followed by GC/MS using capillary columns and selected ion monitoring was used for quantitative analysis. In an initial survey, individual compound concentrations were determined for five PAH in the range of 1 to 300 ppb and for five phenols in the range of 10 to over 1000 ppb.

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 consisting of two concentration levels each of three mixtures and containing a total of twenty-one deuterated compounds have been prepared and delivered to EPA. Work is in progress on establishing the chemical and isotopic purity of compounds which are to be used for modified internal standards sets to be delivered by the end of the year.

Research planned for the coming year includes: continuation of the ongoing projects related to environmental problems with extension to new matrices and the investigation of negative ion chemical ionization for quantitation; further development of the isotope dilution definitive methods for urea and creatinine, initiation of work on methods for triglycerides and digoxin, and implementation of improvements to the instrumentation used; continued refinement and application of the NBS developed liquid chromatography/mass spectrometry system; and, for the competence building program, completion of major equipment installation and modification followed by the start of investigations of the chemistry of several laser induced and collision induced reactions of larger (molecular weights in the range of about 1000 daltons) organic molecules.

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

6. Spectroscopy Group: Overview

During the past year, the Spectroscopy Group has actively pursued research in organic analysis by nuclear magnetic resonance (NMR) spectroscopy, polarimetry, and luminescence techniques, and has expanded its competence in the areas of (1) total carbon analysis by infrared methods and (2) the synthesis of bioorganic intermediates needed in current research programs.

Our recent work in the area of microspectrofluorimetry includes demonstration of reproducibility of measurements and photomicrographs of Tb/Eu doped fluorescent glass beads for a final report to the sponsoring agency, and preliminary measurements on fluorescent standards for cracked plate analysis and on diffusion of anti-oxidants in polyethylene (in collaboration with the Polymers Division).

Preliminary fluorescence measurements with an optical multichannel analyzer, necessary to produce excitation-emission matrices, have indicated the presence of several instrumental and alignment problems in the system. These are currently being studied in both static and flowing modes.

In connection with a Department of Energy program for analysis of waste water, new instrumentation for analysis of total carbon content by infrared techniques has been acquired and installed. The method is based on infrared detection of carbon dioxide produced by combustion of the sample and has been applied initially to DOE waste waters and an angiotensin SRM. Total carbon measurements on Washington dust samples and leachates from blood storage bags are also in progress.

As part of an international effort to assure uniform methods of sugar analysis, the optical rotatory dispersion of standard quartz control plates has been investigated with the NBS high precision polarimeter, and the results correlated by means of a four-parameter equation.

Activities of the Group in SRM certification include completion of the sodium pyruvate and sucrose SRM's, determination of the ultraviolet absorptivities and fluorescence spectra of 16 polynuclear aromatic hydrocarbons (PAH) to be used in SRM 1647 (Priority Pollutant PAH in Acetonitrile), and completion of the testing of candidate materials for the tripalmitin SRM. Procurement and packaging of the latter SRM are complete, and certification measurements are underway.

Efforts this year in the area of NMR instrumentation have included enhancement of the capability of the high field facility of the National Measurement Laboratory by installation of a broad band probe and preamplifier, and implementation of correlation NMR spectroscopy and the Redfield pulse sequence. The broad band components give us a broad range of heteronuclear capability in the high frequency range (45-165 MHz; ^{137}Ba-^{31}P), whereas the correlation and Redfield techniques permit improved suppression of strong solvent signals, for example, the water signal from aqueous solutions of biomaterials.

New methods for analysis of antibiotics by NMR are of considerable interest to the pharmaceutical industry. In research designed to explore the nitrogen-15 NMR capabilities of the WM-400 high field spectrometer, we have studied the structural and conformational analysis of the fortimicin and neomycin series of antibiotics. As a result of this collaborative research with an NAS/NRC postdoctoral research associate, a new method for analysis of the fortimicin series has been developed that is based on interpretation of proton coupled nitrogen-15 spectra obtained by suppression of NH proton exchange in trifluoroacetic acid solutions. Studies of neomycin B and its components by high field proton and nitrogen-15 NMR and gadolinium cryptate spin-labeling techniques have led to definition of the complete solution conformation of neomycin B, and the measurement of pK_a values for individual nitrogens in the antibiotic from nitrogen-15 NMR titration curves has been used to characterize the major ionic form present in neomycin sulfate preparations.

As part of another postdoctoral research associate project directed toward the synthesis and analysis of anti-tumor nucleosides, a new, efficient synthesis of 2-amino-oxazoline intermediates has been delineated which involves the reaction of glycosylamine derivatives with cyanamide. The method has been applied to the preparation of derivatives doubly labeled with nitrogen-15, and the products have been characterized by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy, mass spectrometry, and reversed-phase HPLC.

During the past year, high field proton NMR has also been used for characterization of compounds of interest to research projects in other Groups in the Division and in other Centers. This has included leachables from silicone and polyurethane implant materials, proposed antiepilepsy drug standards--valproic acid, tegritol, and cyheptamide, a dinitrophenyl derivative prepared for use in the immunoassay of nitrophenols, analysis of the kinetics of the alkaline degradation of NAD and characterization of the products of accelerated degradation of solar heat exchange fluids.

By means of two-dimensional, proton NMR at 400 MHz, the complex 12-spin systems of α- and β-D-glucose (the principal components of SRM D-glucose) have been analyzed completely for the first time. Two-dimensional (2D) NMR spectroscopy has also been used to examine fortimicin B, and the purity of digoxin and digitoxose, studies which are also expected to indicate the feasibility of a complete analysis of the complex proton NMR spectra of digoxin. Digoxin is a candidate SRM and an analyte for which a "definitive" method for serum analysis is needed.

With the eventual delivery of an advanced pulse programmer for high field NMR, we look forward to extension of our analytical capability into heteronuclear, two-dimensional techniques and into sensitivity enhancement by cross polarization methods. In the future, the availability of a broad band probe will permit the NMR analysis of other low abundance, "organic" nuclei such as ^{2}H and ^{17}O, together with a range of metal nuclei.

Future plans in the area of low temperature fluorescence include the use of a helium cryostat to facilitate development of quantitative matrix isolation and Shpol'skii spectroscopic techniques.

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

B. Selected Technical Accomplishments
(Organic Analytical Research Division)

1. Relationships Between Liquid/Liquid Partitioning and Retention in Reversed-Phase Liquid Chromatography

Despite the heavy use of high-performance liquid chromatography in analytical chemistry, we lack the capability to utilize this chromatographic technique to its maximum potential because of the absence of a thorough understanding of the physico-chemical foundations for chromatographic retention and selectivity. In order to better understand chromatographic retention and selectivity, we are using polynuclear aromatic hydrocarbons (PAH) as molecular probes to determine the roles that both the stationary and mobile phases play in the retention mechanisms of reversed-phase high-performance liquid chromatography. The present work is an attempt to relate reversed-phase retention to the simple thermodynamic partitioning between _n_-heptadecane (C-17) and acetonitrile/water mixtures.

On partition between C-17 and aqueous acetonitrile, the following relationship was found to be valid for all PAH examined:

$$\ln K' = X(\ln K'_{CH_3CN} - \ln K'_{H_2O}) + \ln K'_{H_2O} \qquad [1]$$

where K' is the molar-partition coefficient between C-17 and the aqueous acetonitrile, K'_{CH_3CN} and K'_{H_2O} are the molar partition coefficients for pure acetonitrile and pure water, and X is the volume fraction acetonitrile. Since $\ln K'_{CH_3CN} - \ln K'_{H_2O}$ is equivalent to the natural log of the partition coefficient between water and acetonitrile, this term is independent of the other phase and is dependent only on the PAH and the temperature.

Reversed-phase liquid chromatography of the same PAH on both monomeric and polymeric octadecylsilane (C-18) columns yielded a similar relationship for the molar specific capacity k' and the volume percent acetonitrile.

$$\ln k' = X(\ln k'_{CH_3CN} - \ln k'_{H_2O}) + \ln k'_{H_2O} \qquad [2]$$

The $\ln k'_{CH_3CN} - \ln k'_{H_2O}$ term is independent of column type and equivalent to the corresponding partition term for each PAH.

This equivalence of solvent effects between the C-17 partition model and reversed-phase C-18 columns suggests that differences of selectivity between columns are due to innate differences in the stationary phase and not to "salting out" effects from the solvent. Plots (Figures 17A and 17B) of the partition coefficient K vs. the specific capacity k' for each individual PAH differ significantly between monomeric and polymeric C-18 columns. The monomeric column appears to be selective on the basis of aromatic carbon number alone, while the polymeric column appears to be selective on both an aromatic carbon number and shape basis. For six unsubstituted PAH on the polymeric column, a relationship is being investigated between the length-to-breadth ratio, L/B, aromatic carbon number, n, and the apparent phase ratio, ϕ (slope of K vs. k' plot). (Preliminary work suggests that for the monomeric column $\phi = A'n + B'$.) Further

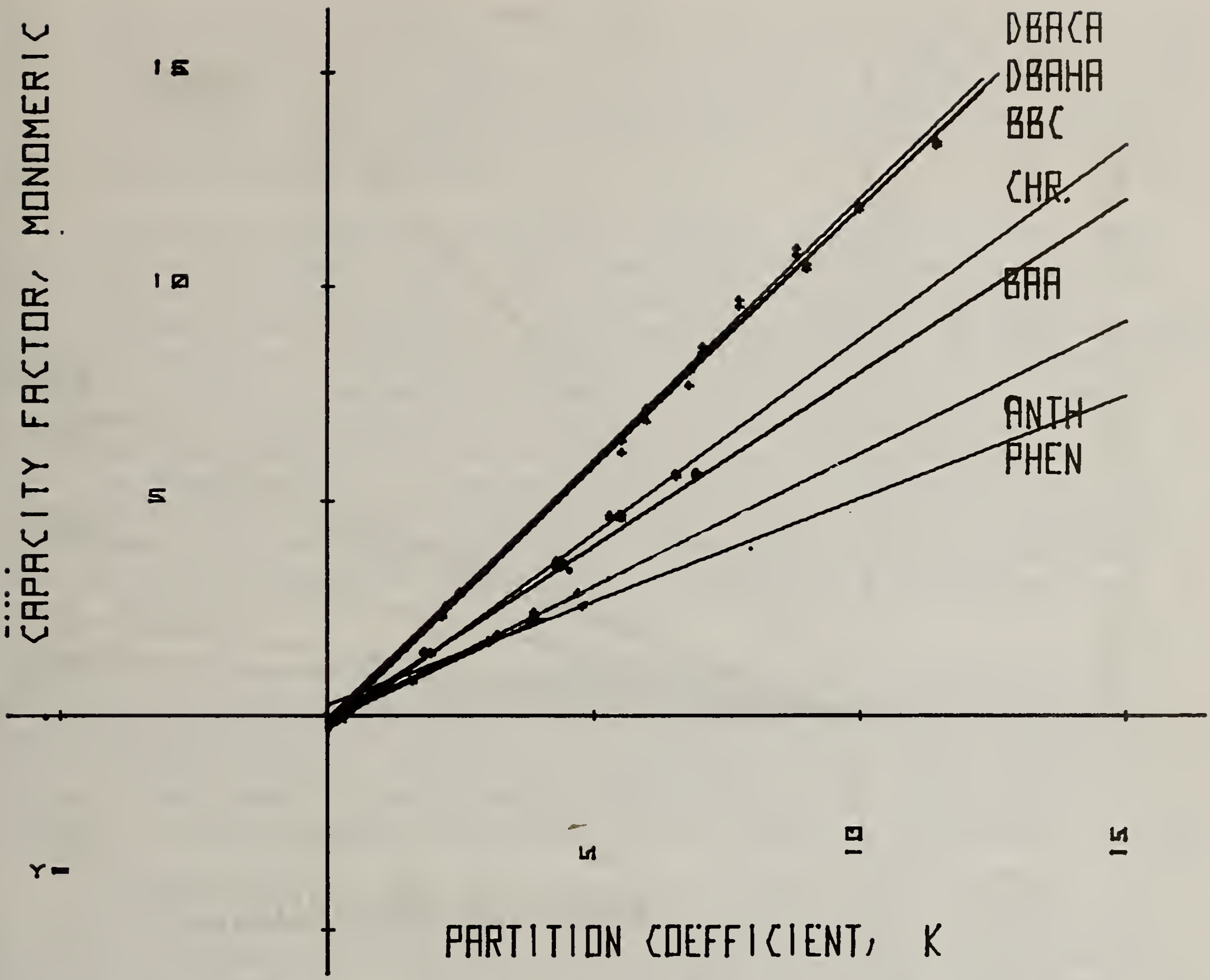

Figure 17A. Abbreviations. DBACA = Dibenz[a,c]anthracene, DBAHA = Dibenz-[a,h]anthracene, BCC = Benzo[b]chrysene, CHR = Chrysene, BBA = Benz[a]anthracene, ANTH = Anthracene, PHEN = Phenanthrene.

refinements to this model are necessary using data from other PAH including methyl-substituted PAH.

If these relationships prove valid for additional PAH, capacity factors and, hence, selectivities can be predicted for polymeric columns from monomeric column data and vice versa.

Additional work on low, average, and high coverage polymeric columns suggests that the retention process is not due to any single mechanism but a mixture of two or possibly more processes. If a relationship can be found between column coverage, retention, and molecular parameters such as L/B and n, the possibility exists for tailoring columns to specific PAH separations for both regular and multidimensional chromatography.

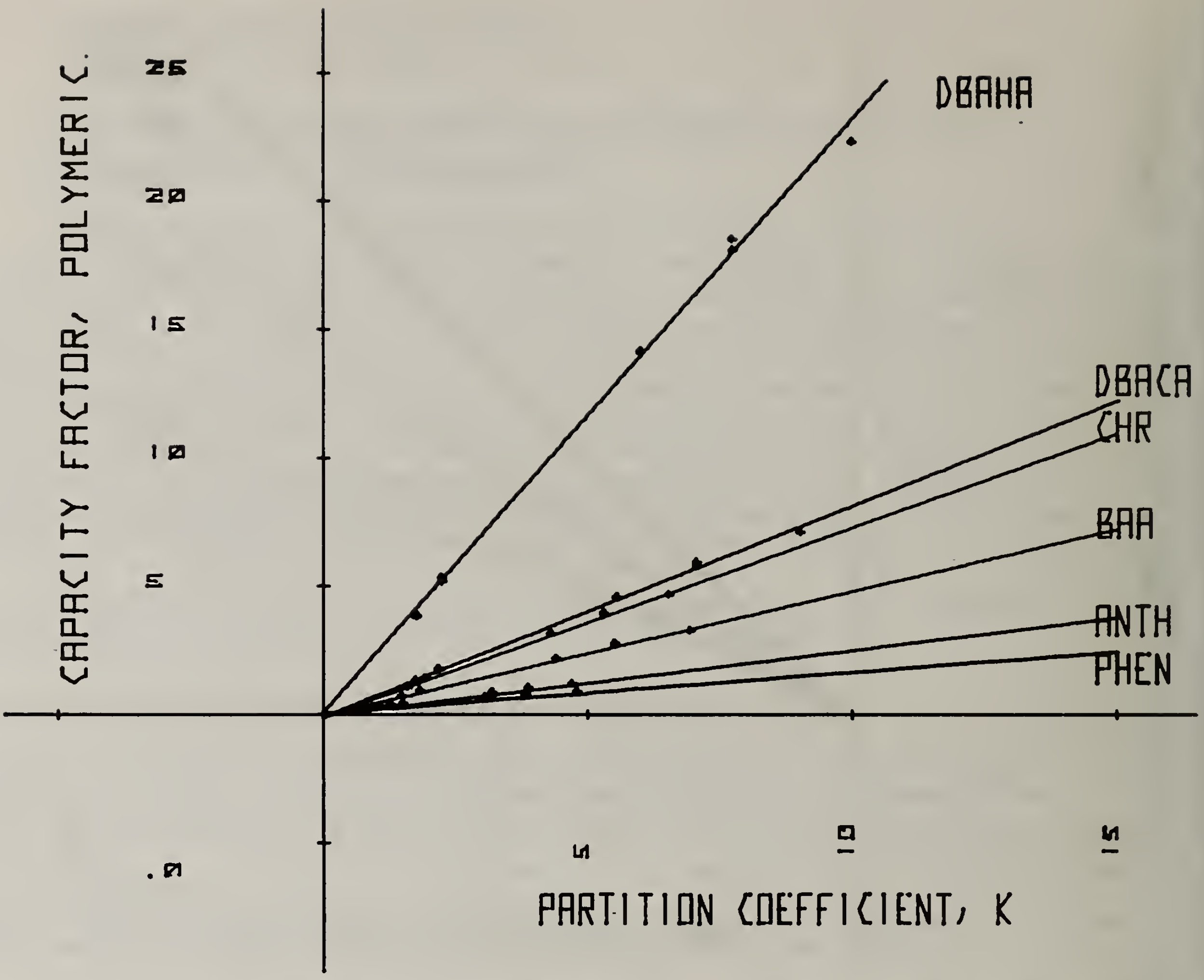

Figure 17B. Abbreviations. DBACA = Dibenz[a,c]anthracene, DBAHA = Dibenz[a,h]anthracene, BCC = Benzo[b]chrysene, CHR = Chrysene, BBA = Benz[a]anthracene, ANTH = Anthracene, PHEN = Phenanthrene.

W. E. May, P. A. White, S. A. Wise

2. Development of an On-Line Multidimensional HPLC System for Quantitative Analysis of Individual Constituents in Complex Samples

The success of the quantitative and qualitative chemical analysis of individual compounds in complex mixtures is dependent upon the resolving power of the analytical system used. Both reversed-phase and normal-phase high-performance liquid chromatography (HPLC) are useful for the separation of organic compounds, yet even the most selective and efficient HPLC columns currently available are unsuccessful in resolving all the components in complex mixtures. The determination of individual species generally requires the use of several chromatographic modes of analysis and/or selective detection. In the past we have advocated the use of normal-phase HPLC on a polar chemically bonded amine phase for the separation of polycyclic aromatic hydrocarbons (PAH) based on the number of aromatic carbons, followed by a separation of the various PAH isomers and/or alkyl-substituted PAH in a given fraction by reversed-phase HPLC. This sequential HPLC method has been employed to quantify selected PAH in several virgin and used lubricating oils, a shale oil, a coal liquid, and a petroleum crude. We are currently extending this method to include nitrogen and sulfur heterocyclic compounds as well as amino- and nitro-substituted PAH.

The off-line multidimensional HPLC analytical procedure [1] previously developed by our group involves the collection of the desired fraction from the normal-phase column, evaporation of the solvent to near dryness, and redissolution of the fraction in an appropriate solvent for the final reversed-phase determination. Disadvantages of this method include: (1) the manipulation of small (20-1000 μL) volumes of eluent which can lead to possible sample contamination and/or losses due to either volatilization or adsorption on container walls; (2) the variability of the volume from which aliquots are taken requires the use of volume correction factors; (3) degradation of the system detection limits is observed since only a fraction of the eluent can be injected onto the reversed-phase analytical column; (4) the high demand on operator time increases the cost of the analysis since the approach is not easily automated.

To eliminate some of these disadvantages, an on-line system coupling a normal-phase chromatographic system to an analytical reversed-phase system has been designed (see figure 18). This system allows for the concentration of a selected fraction from the normal-phase HPLC column on a concentrator column. The solvent is then purged with nitrogen and the concentrator column coupled to a reversed-phase system where the fraction can be further separated.

To demonstrate the applicability of this on-line system for the analysis of PAH in complex matrices, samples of NBS SRM 1580 (Organics in Shale Oil), a solvent refined coal liquid, and a Wilmington crude oil were analyzed for several individual PAH. The results of the multidimensional on-line analysis are listed in Table 13 along with the certified values for SRM 1580 and the earlier off-line sequential HPLC values. No statistical bias is noted between the values, and the precisions of the on-line and off-line methods are comparable.

We are currently extending this system to include other groups of compounds.

Reference

[1] Wise, S. A.; Chesler, S. N.; Hertz, H. S.; Hilpert, L. R.; May, W. E. Anal. Chem. 49: 2306; 1977.

W. E. May, W. J. Sonnefeld, S. A. Wise

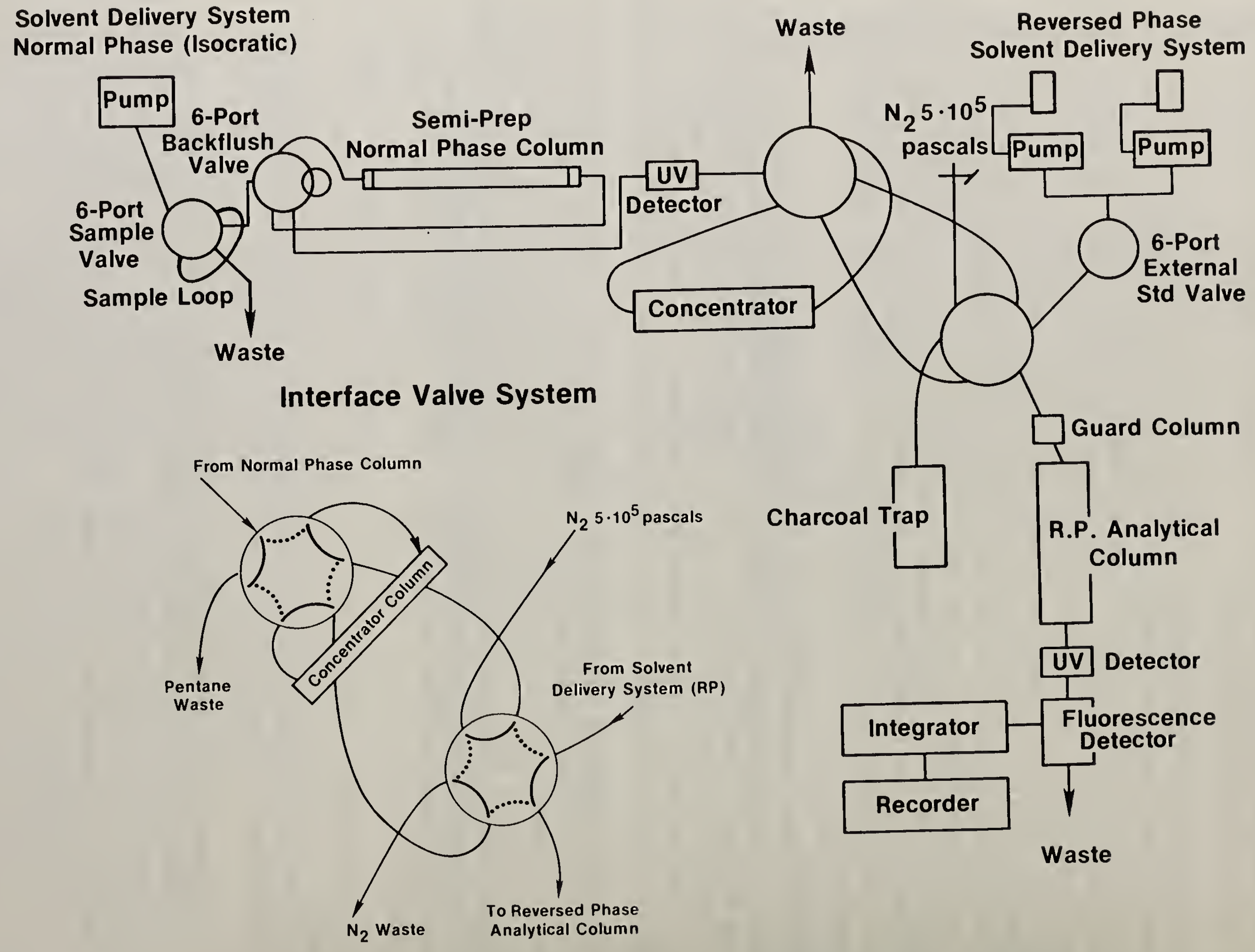

Figure 18. On-line multidimensional system.

Table 13. Comparison of On-Line Multidimensional Results with Off-Line Results.

Compound	Multidimensional HPLC (on-line)[a]	Multidimensional HPLC (off-line)[a]	Certified
	SRM 1580 (Shale Oil) (Concentration in μg/g)		
Fluoranthene	53.8 ± 3.5 (3)[b]	53 ± 2 (9)	54 ± 10
Pyrene	109.7 ± 7.1 (3)	107 ± 8 (10)	104 ± 18
Perylene	2.32 ± .15 (5)	3.9 ± .6 (11)	3.4 ± 2.2
Benzo[a]pyrene	20.7 ± 2.2 (8)	23 ± 1 (8)	21 ± 6
	SRC II Coal Liquid (Concentration in mg/g)		
Fluoranthene	3.15 ± .04 (3)	3.3 ± .16 (3)	
Pyrene	6.65 ± .05 (3)	6.0 ± .2 (3)	
Perylene	0.024 ± .002 (3)		
Benzo[a]pyrene	0.133 ± .008 (5)	0.134 ± .007 (3)	
Benzo[e]pyrene	0.153 ± .006 (3)	0.143 ± .005 (3)	
Benzo[k]fluoranthene	0.062 ± .001 (5)		
	Wilmington Crude Oil (Concentration in μg/g)		
Fluoranthene	2.4 ± .3 (3)	3 ± 1 (3)	
Pyrene	14.8 ± 2.2 (3)	14 ± 2 (3)	

---

[a] Uncertainty is 1 standard deviation.

[b] (n) indicates the number of replicate measurements.

3. Methods for the Determination of Selected Polycyclic Aromatic Hydrocarbons and Aza-arenes on an Urban Air Particulate Sample and SRM Certification of the Sample

Many regulatory programs of the U.S. Government emphasize the need to collect data on the concentration, distribution, and personal exposure to organic pollutants in air. Organic air pollutants of particular interest, because of their ubiquitous nature and carcinogenic properties, are the polycyclic aromatic hydrocarbons (PAH). At NBS, two large samples of urban air particulate material [Standard Reference Material (SRM) 1648 "Urban Air Particulate Matter" (from St. Louis, MO) and urban particulate matter (from Washington, DC)] have been used for the development of analytical methods for the characterization and quantitation of PAH extracted from them. SRM 1648, which is issued in 2-g quantities, is not certified for organic constituents. However, a number of analysts have expressed interest in the organic constituents in this SRM for use in analytical methods evaluation, intercalibration, and biological testing studies. As a result, NBS will issue 10-g quantities of the Washington urban particulate matter as SRM 1649 certified for the concentrations of ten major PAH. During the past year, the analytical methods [i.e., extraction, isolation, and gas chromatographic (GC) and high-performance liquid chromatographic (HPLC) methods for analysis] have been developed for the certification of SRM 1649.

The extraction of air particulate matter with an organic solvent system (e.g., methylene chloride or benzene/methanol), using a Soxhlet extractor, results in a complex mixture of organic constituents from which the PAH must be isolated prior to identification and quantitation by GC and HPLC. Prior to analysis by high resolution capillary gas chromatography, the PAH were isolated from the complex organic extract (obtained with 1:1 benzene/methanol) using a solvent-solvent partition of N,N-dimethylformamide (DMF) and water to remove aliphatic hydrocarbons, followed by a normal-phase HPLC separation to remove the more polar aromatic constituents such as aza-arenes. Quantitation of the selected PAH was relative to an internal standard, 1-methylpyrene, added to the sample prior to extraction.

In the HPLC analyses, quantitation was accomplished using fluorescence detection to achieve the selectivity necessary to quantitate individual compounds in the complex mixture. The sample was extracted with methylene chloride; then the extract was partitioned between cyclohexane and nitromethane to remove some interfering constituents prior to analysis. Because of the selectivity of the HPLC fluorescence detection for PAH compared to the universal flame ionization detection for GC, a less rigorous PAH isolation procedure was used for the HPLC analysis than for the GC (i.e., cyclohexane/nitromethane partition vs. cyclohexane/DMF/water partition and HPLC). This selectivity is illustrated in figure 19 for the HPLC analysis of the air particulate extract. In the upper chromatogram, a UV absorption detector is used for detection, whereas in the middle and lower chromatograms six different fluorescence excitation and emission wavelength combinations are employed to optimize the selectivity/sensitivity for various PAH. HPLC quantitation is based on an internal standard of 7-methylfluoranthene. Preliminary HPLC and GC analyses indicate the following concentration ranges for several major PAH; pyrene, fluoranthene, benzo[b]fluoranthene,

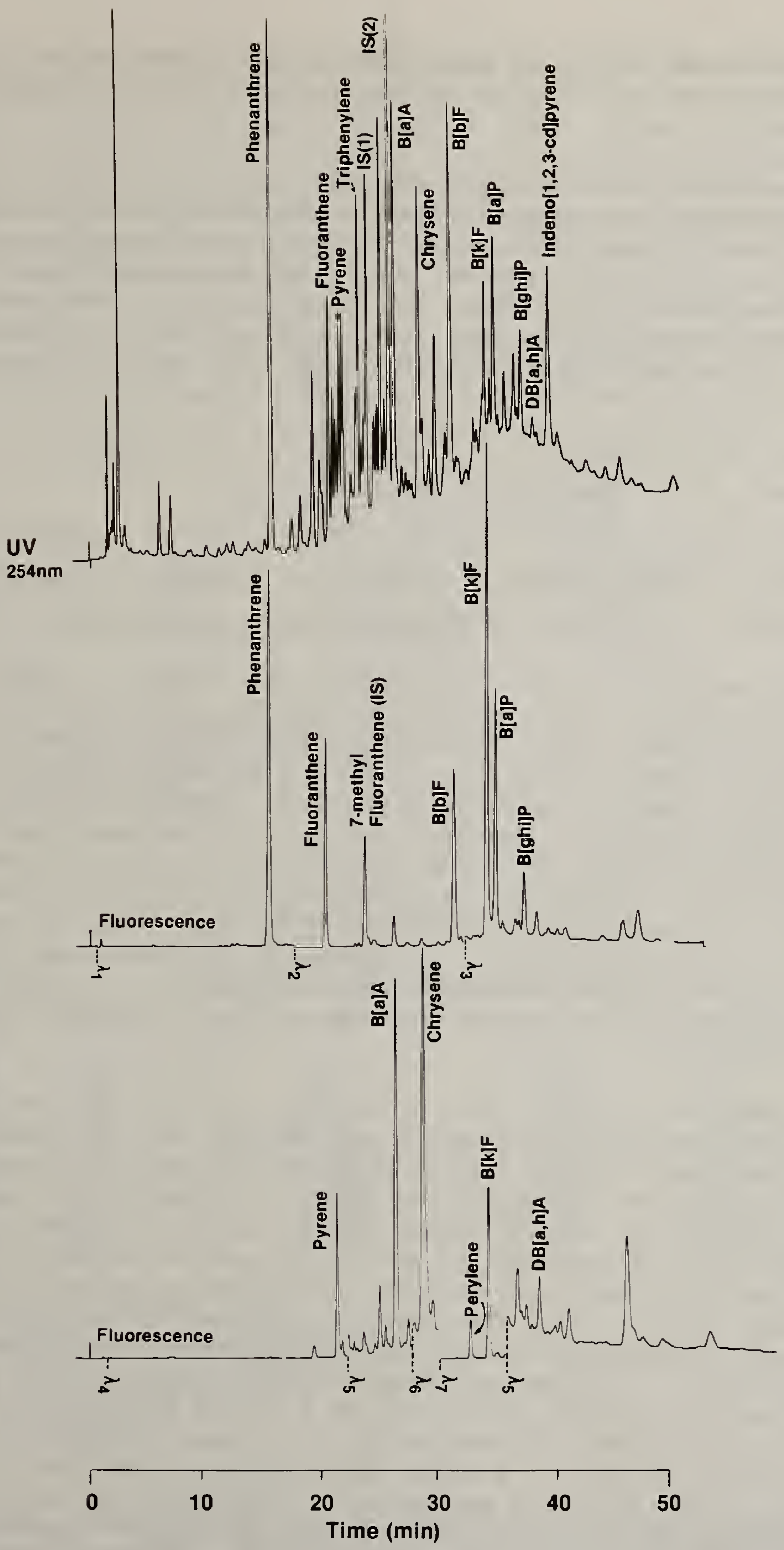

Figure 19. Liquid chromatographic separation of PAH isolated from air particulate matter with UV detection (upper chromatogram) and fluorescence detection at various excitation and emission wavelengths (middle and lower chromatograms).

benzo[ghi]perylene, 5-6 µg/g; phenanthrene, benz[a]anthracene, chrysene, benzo[k]fluoranthene, 3-5 µg/g; and perylene and dibenz[a,h]anthracene, ∿0.5 µg/g.

The Washington urban particulate material is also being used to develop analytical methods for the isolation and characterization of other classes of polycyclic aromatic compounds in air particulate material in addition to the major PAH, i.e., nitrogen, sulfur, and oxygen heteroaromatic compounds. Currently, research is focused on the determination of aza-arenes using an acidic extraction, HPLC clean-up, and GC analysis with a nitrogen specific detector. Preliminary analyses indicate that the major aza-arenes are quinoline, isoquinoline, and alkyl homologs of these compounds.

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4. Methods for the Analysis of Polynuclear Aromatic Hydrocarbons (PAH), Amino-PAH, and Phenols in Alternate Fuels and Effluents

Energy demand in the U.S. has intensified efforts to develop alternate energy sources such as coal, oil shale, and tar sands. Contamination of the large amounts of water used in the mining and refining operations for some of these processes results in a significant environmental threat. It is, therefore, important that the aqueous effluents be monitored for their toxic organic compound content. Research sponsored by the Department of Energy has continued during FY 1981 on the development of accurate gas chromatographic/mass spectrometric (GC/MS) and high-performance liquid chromatographic (HPLC) methods for the quantitative determination of toxic organic compounds in alternate fuels and effluents. The complexity of these sample matrices requires that the methods be highly specific, and the relatively low concentrations (ppm to ppb) of the analytes demand high sensitivity for accurate quantitation.

Coal gasification, oil shale retorting, and petroleum refinery aqueous effluents were analyzed for phenolic and PAH species. A simple organic extraction was developed to isolate the analytes prior to quantitative determinations by selected ion monitoring GC/MS. Pyrene-d_{10} was used as the internal standard for the PAH determinations and 2-chlorophenol was used for the phenols. Two aliquots of the effluents were extracted with methylene chloride, one at a neutral pH for the PAH and one after acidifying with sulfuric acid to pH 1-2 for the phenols. Aliquots of the concentrated extracts were chromatographed on high-resolution wall-coated open tubular capillary columns. The PAH were separated on a nonpolar 30 m x 0.25 mm SE-30 coated column, the phenols on a polar 20 m x 0.25 mm Pluronics PL-64 column. Selected ion monitoring of characteristic, intense ion(s) in the mass spectrum of each analyte was used to enhance the selectivity and sensitivity of detection. Since no time is wasted scanning portions of the spectrum in which there are either (a) no ions, or (b) ions of low intensity, sensitivity is increased by recording intense ions at characteristic masses and integrating the ion currents. To ensure that the mass spectrometer is measuring the signal at the top of the mass peaks, the ions are monitored in 0.1 amu increments (e.g., for the benzopyrenes, with a nominal molecular weight of

252, ions at m/z 252.0, 252.1, 252.2, and 252.3 are monitored with a dwell time of 100 ms for each ion). The integrated ion currents are plotted versus chromatographic retention time (see figure 20). The single ion records show chromatographic resolution of the analytes from non-analyte components in the sample extract which also yield ions at m/z 252. The individual analyte concentrations are then determined from the analyte and internal standard peak areas and experimentally determined relative response factors. Five PAH and six phenols were determined in aqueous effluents from coal gasification, oil refinery, and oil shale processes. The results of these determinations are shown in Tables 14 and 15. Values represent an average of two determinations. The individual determinations differed by 10 percent or less.

Table 14. Polynuclear Aromatic Hydrocarbons in Effluents.

	Analyte Concentration (ppb)				
Sample	Fluoranthene	Pyrene	Benzo[e]pyrene	Benzo[a]pyrene	Perylene
CG-04	11.6	11.0	0.92	1.6	0.5
CG-06	303	281	30	58	18
OR-21	<1.0	<1.0	<1.0	<1.0	<1.0
OS-43	<1.0	<1.0	<1.0	<1.0	<1.0

Notes: CG = coal gasification effluent
OR = oil refinery effluent
OS = oil shale effluent

Table 15. Phenols in Effluents.

	Analyte Concentration (ppb)					
Sample	Phenol	2,6-DMP	2,4- and 2,5-DMP	o-Cresol	m-Cresol	p-Cresol
CG-04	1040	27	190	300	16	27
CG-06	730	290	890	490	330	250
OS-42	<10	<10	<10	<10	<10	<10
OS-43	<10	<10	ND	<10	ND	ND
OR-21	<10	<10	<10	<10	<10	<10
OR-23	<10	<10	ND	<10	ND	ND
OR-25	<10	<10	<10	<10	ND	ND

Notes: DMP = dimethylphenol
CG = coal gasification effluent
OR = oil refinery effluent
OS = oil shale effluent
ND = not detected

Several amino-PAH have been determined in an SRC II coal liquid and a Wilmington crude oil sample. 1-Aminonaphthalene and 2-aminoanthracene were determined in the samples using a sequential HPLC procedure. The analytes were isolated from the oil matrices by chromatography on an aminosilane column using ∿45-60 percent methylene chloride-in-hexane as the mobile phase. The analytes were then further separated from other interferences by

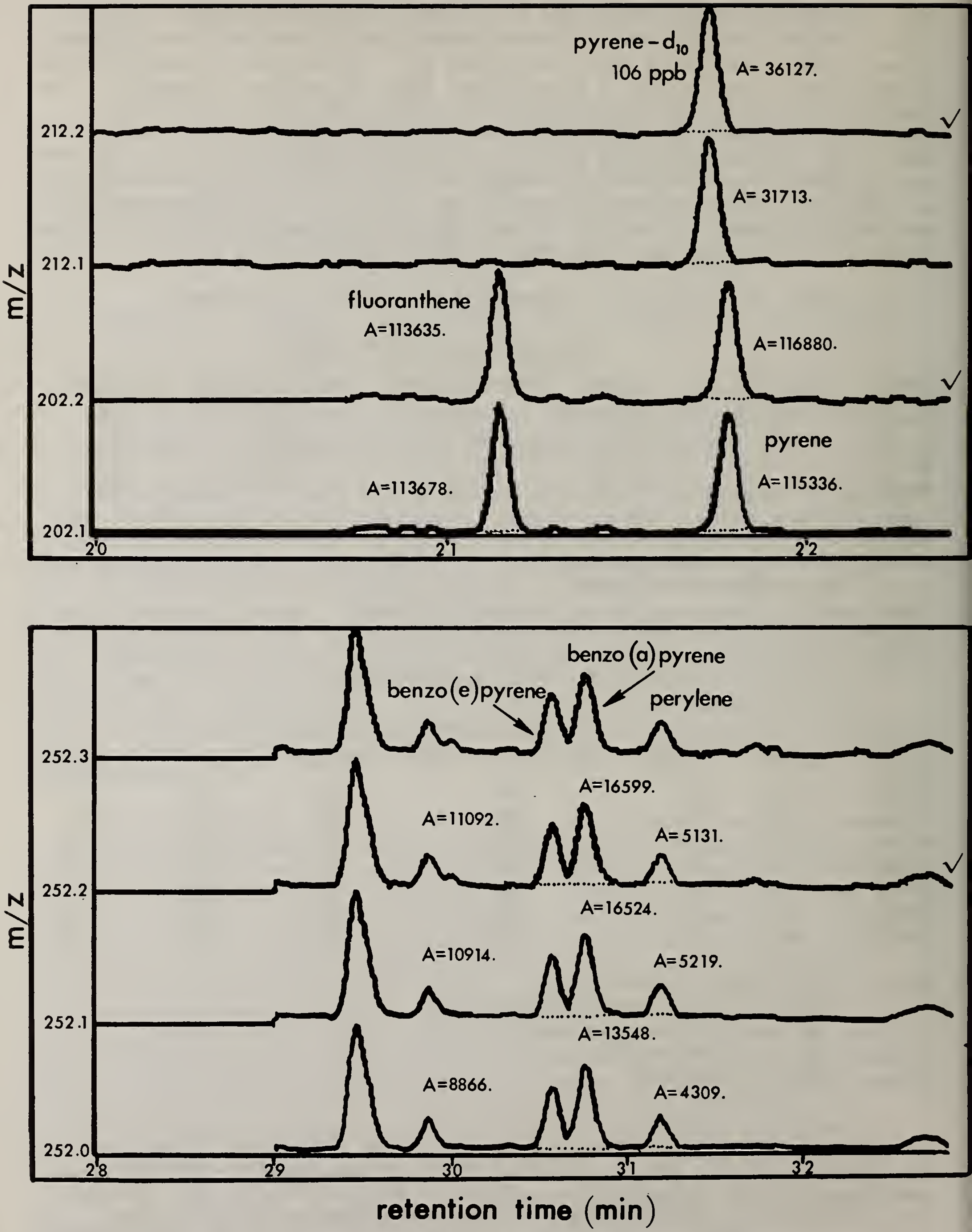

Figure 20. Selected ion chromatogram GC/MS analysis of PAH in coal gasification effluent.

chromatography on a C-18 column with 40 percent acetonitrile in water as the mobile phase. Detection was done spectrofluorimetrically with the excitation and emission wavelengths optimized for each compound. The results of initial analyses are shown in Table 16.

Table 16. Amino-PAH in Fuel Samples (ppm).

Analyte	Wilmington Crude	SRC II Coal Liquid
[illegible]Aminonaphthalene	8	140
2-Aminoanthracene	0.3	13

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5. Methodology for Certification of a Polychlorinated Biphenyl (PCB) in Oil SRM

Polychlorinated biphenyl (PCB) mixtures have been used extensively in this country in high-voltage electrical components. These toxic compounds may be introduced into the environment when the electrical components in which they are contained are repaired or discarded. PCB-containing fluids physically resemble lubricating oil, and there have been instances in which toxic PCB's have been mistakenly added to oils being collected for recycling purposes. Thus, a PCB SRM will find use in the electrical industry where PCB contamination of transformer cooling fluid is of current concern, and in the motor oil recycling (re-refining) industry where inadvertent contamination by PCB-containing fluids is a potential problem.

A Standard Reference Material entitled "Polychlorinated Biphenyls in Oil" (SRM 1581) has been prepared consisting of separate solutions of Aroclor 1242 and Aroclor 1260 (commercial polychlorinated biphenyl mixtures) in a transformer oil and a motor oil base at the 100 ppm (wt./wt.) level.

Two independent analytical methods are being used for the certification measurements. First, quantitative data were obtained from the gravimetric preparation of these solutions. Secondly, a hybrid chromatographic technique developed in our laboratory is utilized that involves both gas chromatography and high-performance liquid chromatography (HPLC). HPLC is used first to remove the major interfering components in the oil sample (see figure 21). The "clean" sample is then separated into its component parts using a nonpolar wall-coated open-tubular gas chromatographic column and selective electron capture detection (see figure 22). Quantitative data are obtained by relating peak areas of three internal standards (PCB isomers are used which are not detected in the Aroclor of interest) to the areas of the PCB peaks of samples and of calibration standards.

In addition to the certification of total PCB content, concentrations of selected PCB isomers in each of the Aroclor solutions will be measured, as well as total chlorine content by neutron activation analysis (R. Fleming, Division 551).

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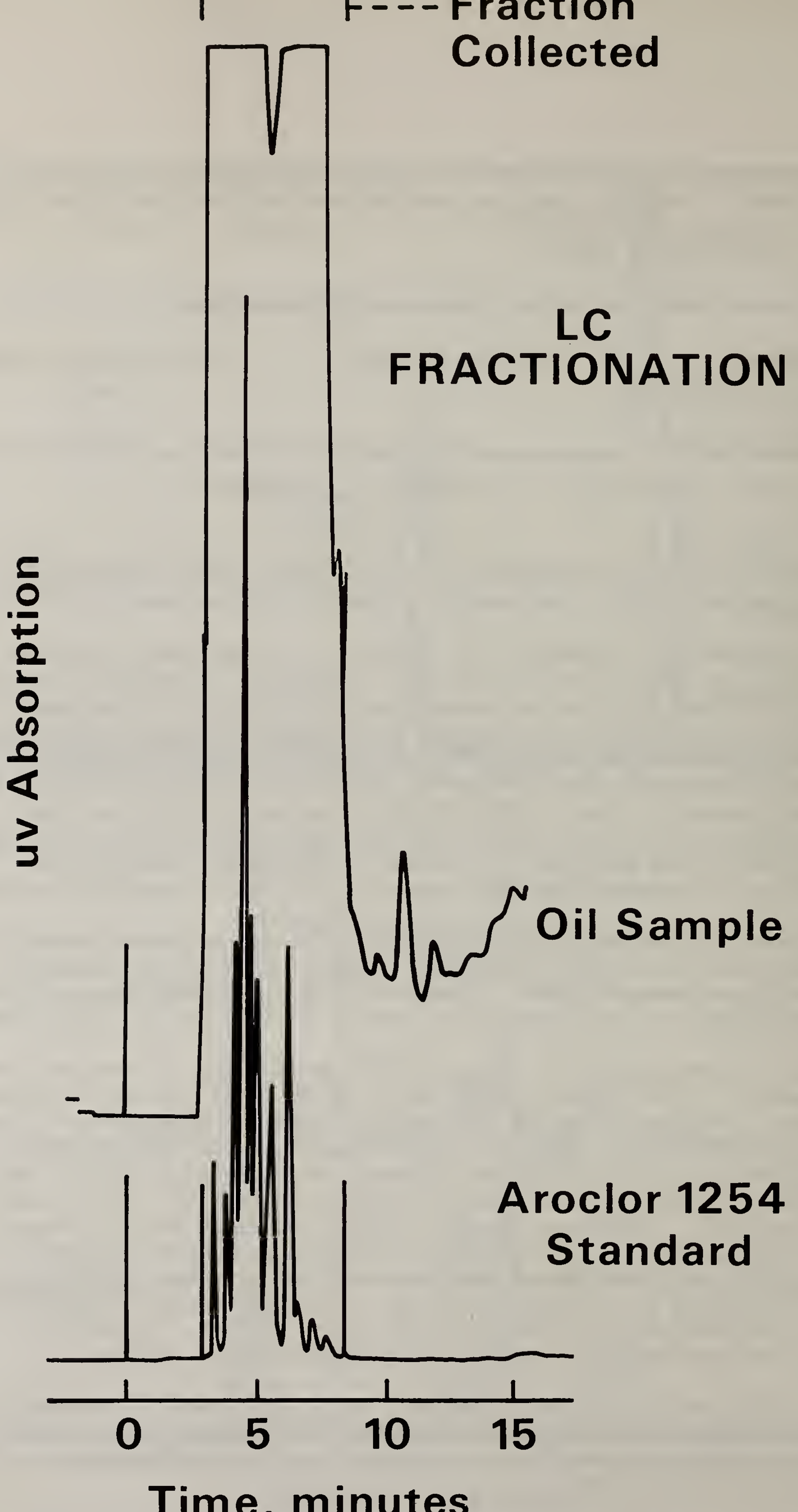


Figure 21. Preparative scale HPLC fractionation of a motor oil sample.

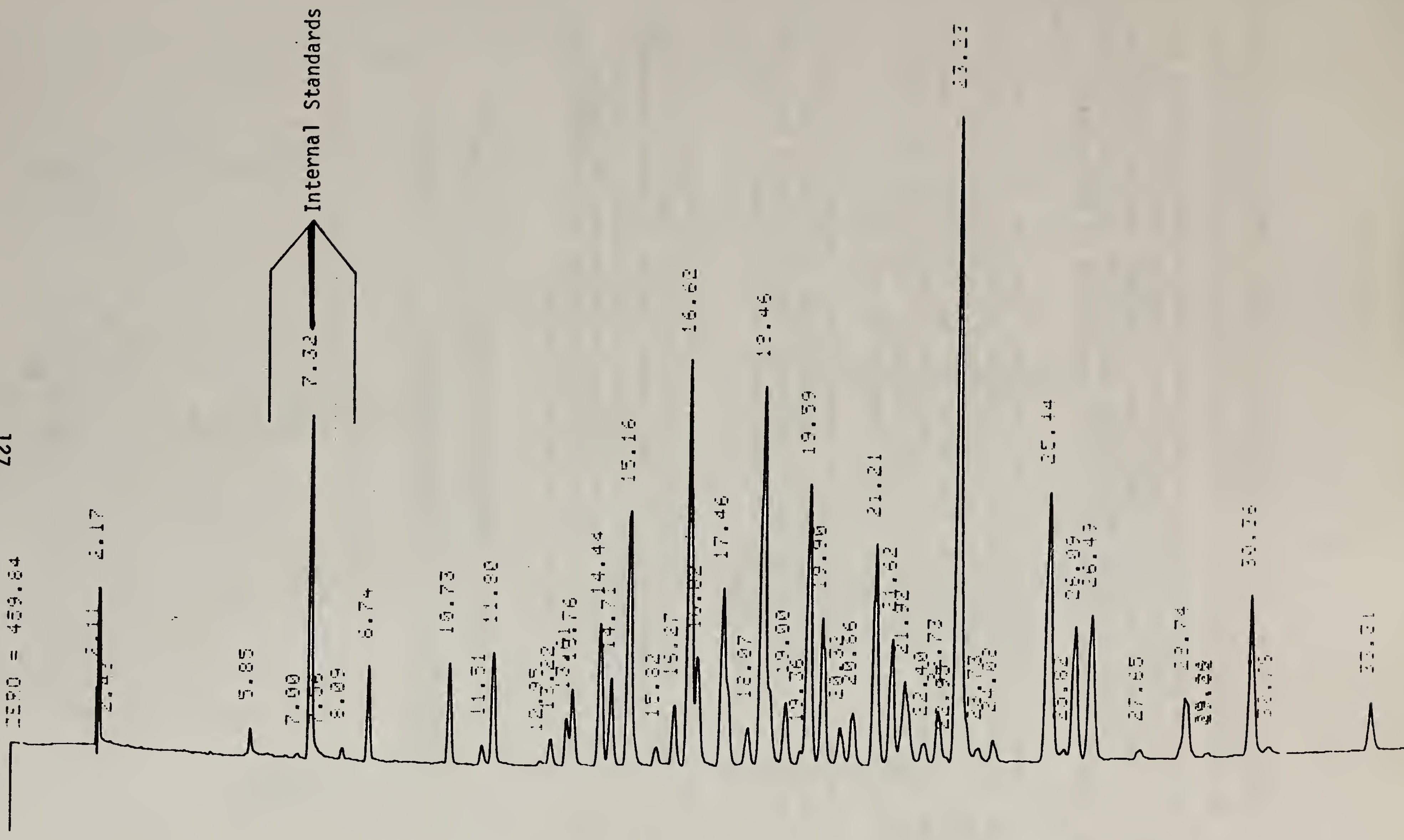


Figure 22. High resolution gas chromatogram (electron capture detection) of the PCB-containing fraction of "Motor Oil Base and Aroclor 1260".

6. Identification of Polychlorinated Biphenyl (PCB) Isomers Using Combined Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectroscopy

During the past year, 42 pure PCB isomers were procured and their gas-phase IR spectra obtained and assembled into a computer data base. Table 17 lists the available spectra by isomer groups. Emphasis has been placed on the tetra- and penta-isomers, due to their abundance in Aroclors 1242 and 1248, some of the most common PCB mixtures encountered in environmental analyses.

All work to date has been on Aroclors 1242, 1248, and 1260. Concentrated solutions of these Aroclors (0.1 percent in methylene chloride) were run on a 30-meter fused silica capillary column, coated with a nonpolar bounded liquid phase (DB-5) to a thickness of 1 µm. The effluent from this column was then run directly into a special low-volume 2 mm x 42 cm gold-plated light pipe (approximately 1.5 cm^3 volume). Injections were made splitless utilizing the solvent effect reported by Grob [1].

A Gran-Schmidt [2] reconstructed chromatogram is shown in figure 23. This represents a "total wavelength" response of the FT-IR to the GC effluent. Examination of the spectra indicated that very few of the peaks were single isomers. However, the peak at data point 153 was identified as 2,4',5-trichlorobiphenyl.

Work is continuing with regard to (1) increasing GC resolution to simplify the IR spectra, (2) obtaining more pure-isomer spectra, (3) deconvoluting multicomponent peaks utilizing library spectra of known components in the peak, and (4) using HPLC fractionation of the Aroclors to reduce chromatographic complexity. Developing these procedures on the complex Aroclor isomer mixtures will provide an excellent model for generic development of GC/FT-IR spectroscopy in analytical chemistry.

Table 17. Available PCB Isomers.

No. of Chlorines	Possible Isomers	In Library
1	3	1
2	12	
3	24	7
4	42	16
5	46	12
6	42	4
7	24	2
8	12	
9	3	
10	1	
	209	42

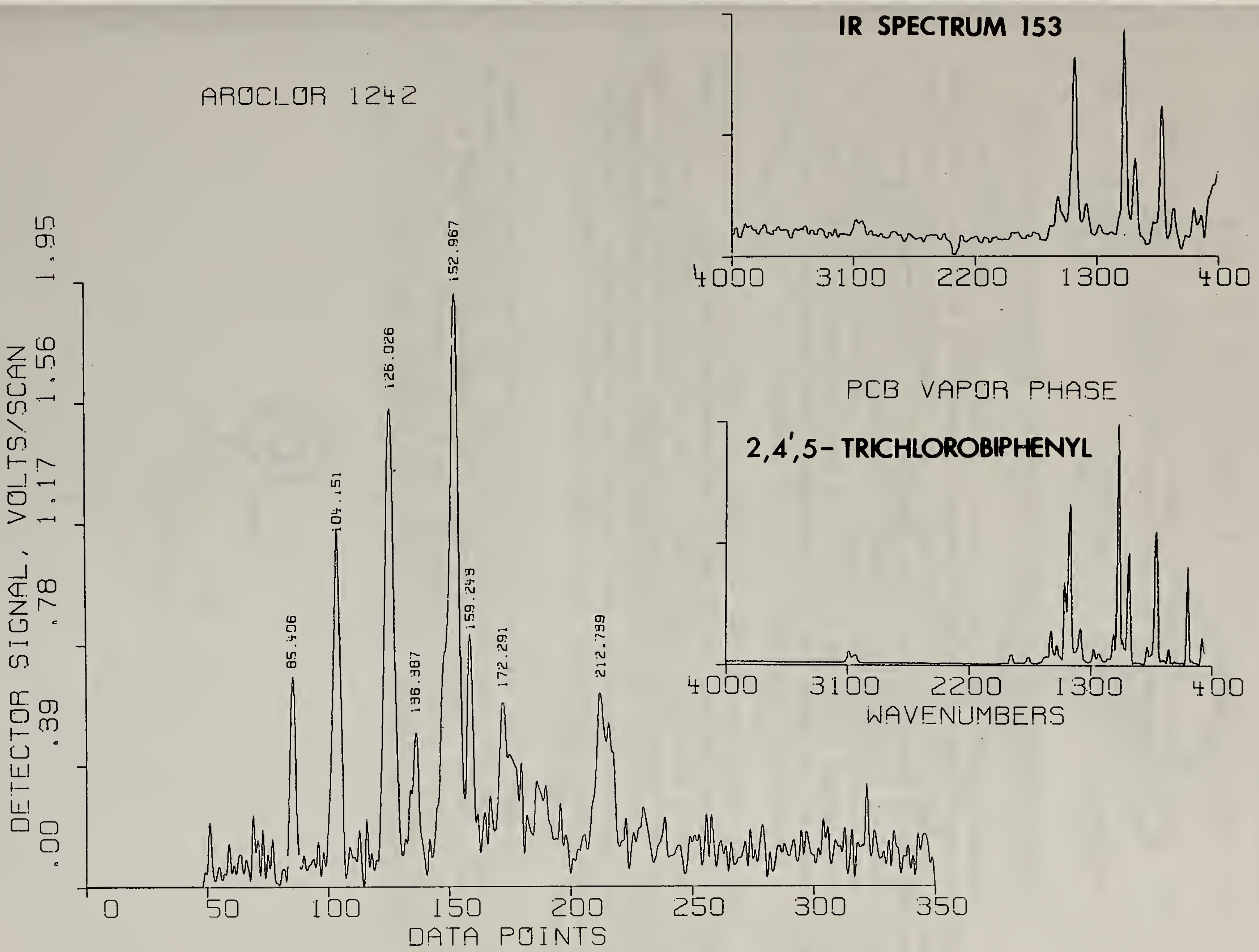


Figure 23. Gran-Schmidt reconstruction of Aroclor 1242 from a 30 meter, DB-5 capillary column. IR spectrum 153 was found to match the library spectrum of 2,4'5-trichlorobiophenyl.

References

[1] Grob, K.; Grob, K., Jr. J. Chrom. Sci. 8: 53; 1974.

[2] Hanna, D. A.; Hangac, G.; Hohne, B. A.; Small, G. W.; Wieboldt, R. C.; Isenhow, T. L. J. Chrom. Sci. 17: 423; 1979.

F. R. Guenther, R. M. Parris

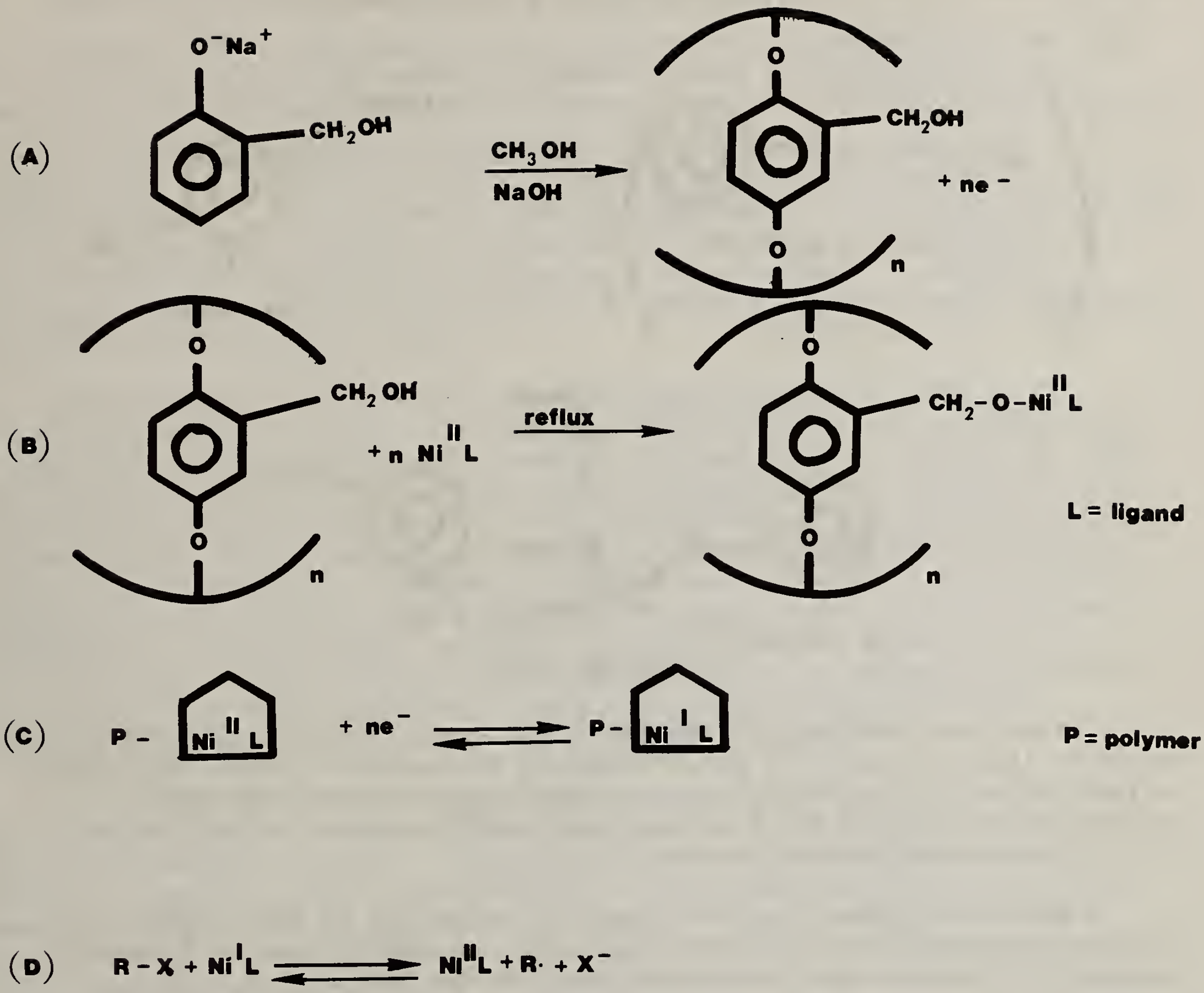
7. Chemically Modified Electrode Detector for Halogenated Hydrocarbons

Halogenated hydrocarbons, such as polychlorinated biphenyls, organochlorine pesticides, and organohalogenated industrial solvents, constitute one of the major classes of hazardous wastes contaminating the environment and comprise a fair portion of the EPA Priority Pollutant List. Most of these types of compounds are presently determined by gas chromatography following solvent extraction to separate and concentrate the analyte. An analytical method is needed which can be applied directly to the sample matrix without the necessity of a pre-separation/concentration step and which also is amenable to field use for on-site analysis.

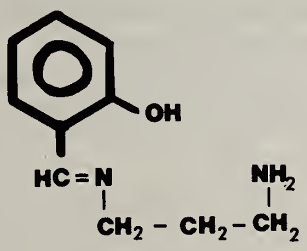
We are interested in the development of chemically modified electrodes, which will electrocatalytically detect organohalide compounds. These chemically modified electrode sensors could allow the selective and sensitive detection of organohalide compounds in the presence of complex matrix interferences. Chemically modified electrodes were fabricated by electrodeposition of a polyphenylene oxide polymer film on Pt or Au substrates. The polymer molecules contain functional groups which are derivatized chemically [see Schemes I(A) and I(B)].

In Scheme I, the solution Ni(II)L/Ni(I)L redox couple has been shown to be electrochemically and chemically reversible. The Ni(I) complex forms an adduct with the R-X species, if present, and subsequent transfer of an electron to the R-X moiety regenerates the Ni(II) complex. The reduction of R-X to X^- and R• proceeds rapidly and catalytically, at -1 to -1.5 volts vs. S.C.E. as opposed to -2.3 volts for the direct reduction of R-X.

Scheme I:

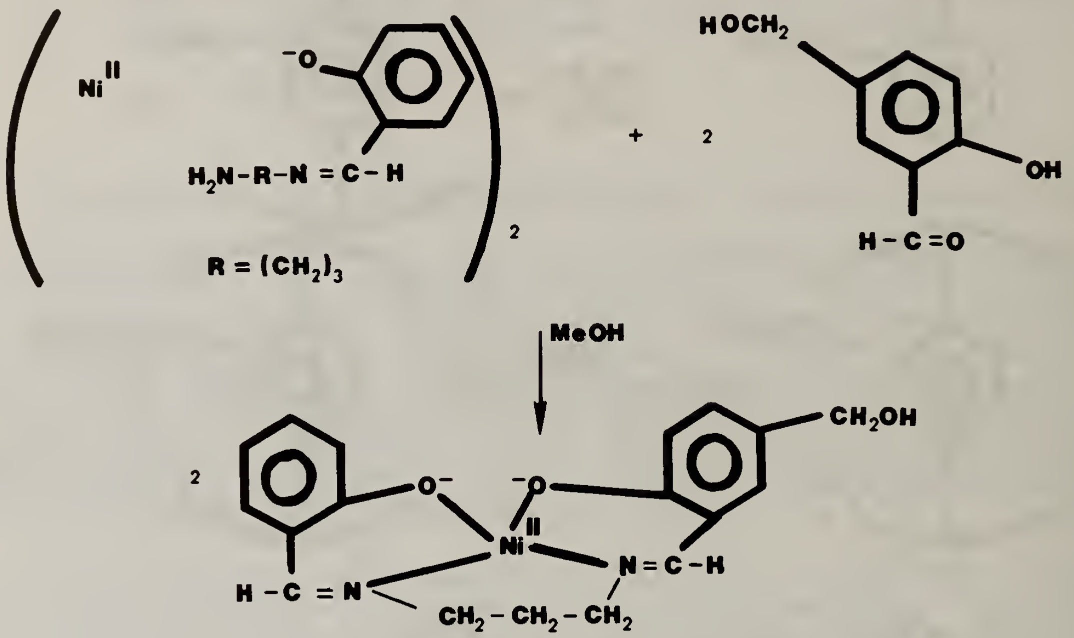


The synthesis of unsymmetrical Schiff-base ligands starts with the synthesis of 1.



1

This molecule is formed by the 1:1 molar condensation of salicylaldehyde with 1,3-diaminopropane. The final synthetic step involves condensation of meta-substituted salicylaldehyde with a nickel complex:



Future work involves (1) further film characterization via surface analysis (ESCA, Raman), (2) electrochemical evaluation of these derivatized polymer films, (3) evaluation of the stability associated with these polymer films, and (4) the electrocatalytic efficiency as a function of film thickness and chemical composition.

A potential spin-off of this research is the use of these chemically modified electrodes for the electrosynthesis of useful products from waste materials. Such a recycling process would follow the scheme:

$$R\text{-}Cl + e^- \xrightarrow{\text{CME}} Cl^- + R\cdot \xrightarrow{R\cdot} R\text{-}R.$$

In other words, dimerization of the hydrocarbon radicals would result in dehalogenated organic compounds possibly of lower toxicity or perhaps commercial value.

E. A. Blubaugh

8. Electrochemical Oxidation of Croconate Salts and Their Implication in Semiconductor Behavior and Electrochromic Displays

As part of the competence building program in electrochemistry, we have been investigating several aromatic compounds based on dicyanomethylene derivatives of croconates (pseudo-oxocarbons of general formula $C_nO_m[C(CN)_2]_{n-m}$). These compounds are intense chromophores and exhibit appreciable electrical conductivity, hence they are ideally suited as models for research in spectroelectrochemistry. From the results of the nonaqueous solution electrochemistry and crystallographic analysis, a mechanism for the electrical conductivity of crystalline potassium croconate violet has been proposed. In addition, it was shown that the intense coloration of croconate solutions can be reversibly altered by electrochemical means.

The solution electrochemistry in N,N-dimethylformamide (DMF) of four croconate dianions indicates that two reversible one-electron transfers occur (figure 24). The first oxidation process is a one-electron abstraction from the dianion to form a stable radical anion followed by a second one-electron oxidation of the radical anion to the neutral molecule. The first oxidation process causes nearly complete extinction of the croconate coloration (see figure 25). The color is completely restored upon reversal of the electrode potential to its rest potential. Although the reaction is relatively slow (compared to a liquid crystal display), the fact that the color is at its full intensity at rest potential means that no power is consumed to produce the color. This result would be of great value for displays that are ordinarily "lit" and only have to be extinguished momentarily.

In considering electron conduction in crystalline organic materials, it is clear that chemical changes during electron conduction could severely alter the conduction process. Although the solution electrochemistry of potassium croconate violet indicates the dicyanomethylene groups are electrochemically active, it is apparent that electron transfer must be initiated and terminated at the alkene bond, since this is the only redox process that leaves the molecule structurally unaltered. However, because of the stacking arrangement, electron migration, illustrated in figure 26, most likely occurs between a dicyanomethylene group and the alkene bond of adjacent unit cells and between dicyanomethylene groups within the unit cell. Electron conduction can be rationalized in the dicyanomethylene group by invoking either a concerted electron transfer or delocalization of the unpaired electron by resonance (resonance forms are depicted in figure 26), each process leaving the dicyanomethylene group intact. The result is the dicyanomethylene group becomes the conduction arm of the molecule while the alkene bond undergoes oxidation/reduction.

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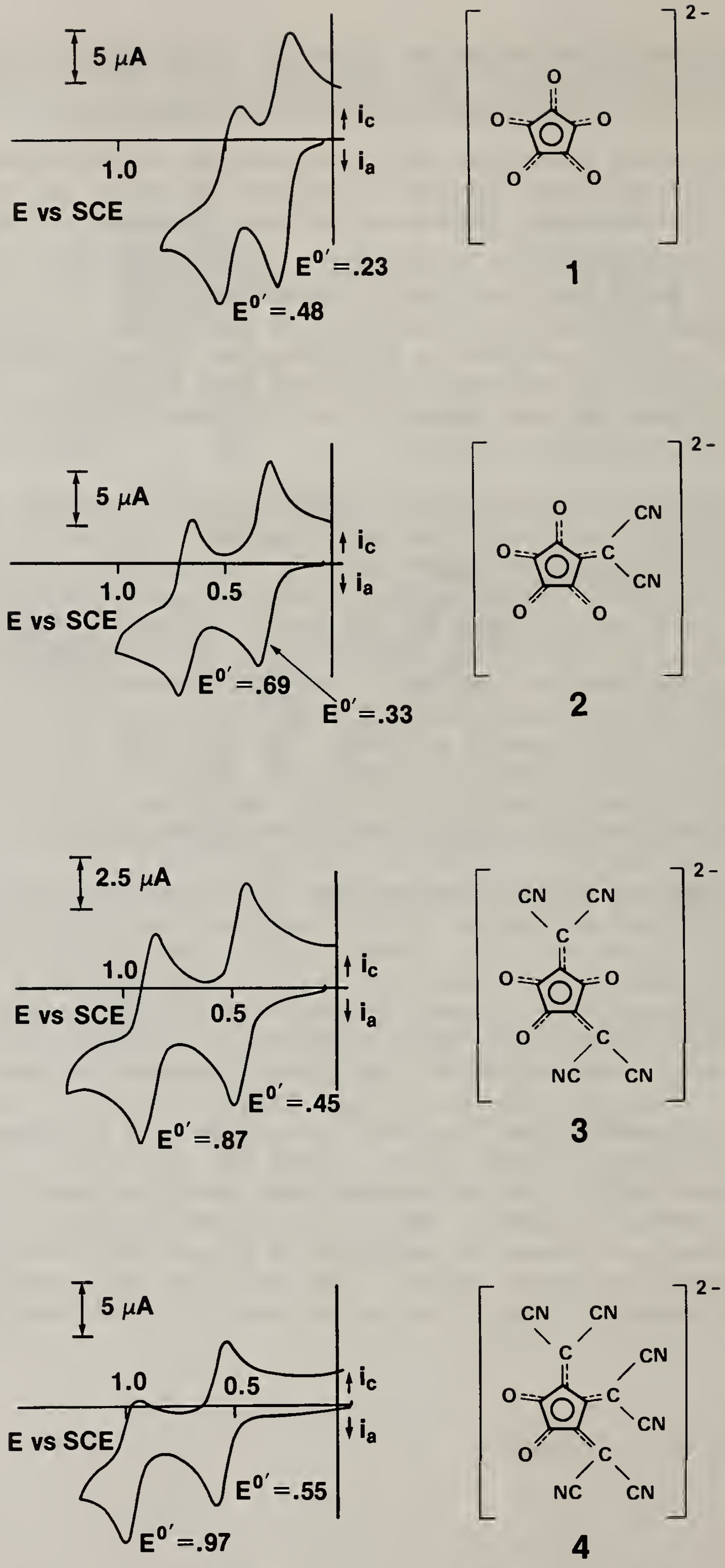


Figure 24. Cyclic voltammetry in 0.5 mol/L TEAP - DMF at 0.05 V/s of croconate (1), croconate orange (2), croconate violet (3), and croconate blue (4).

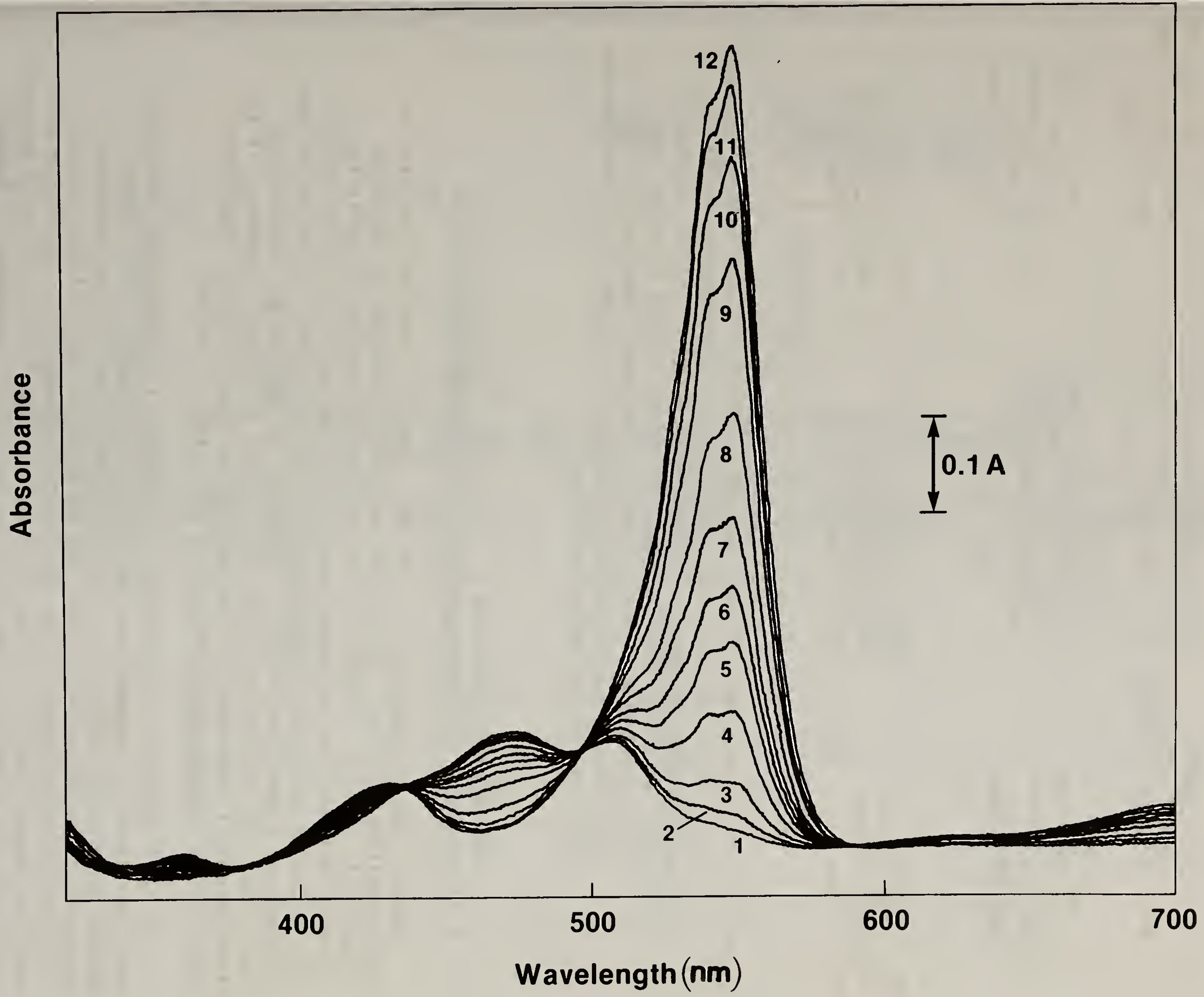


Figure 25. Absorption spectra of croconate violet for potentials of the first oxidation process ranging from (1) fully oxidized to (12) fully reduced.

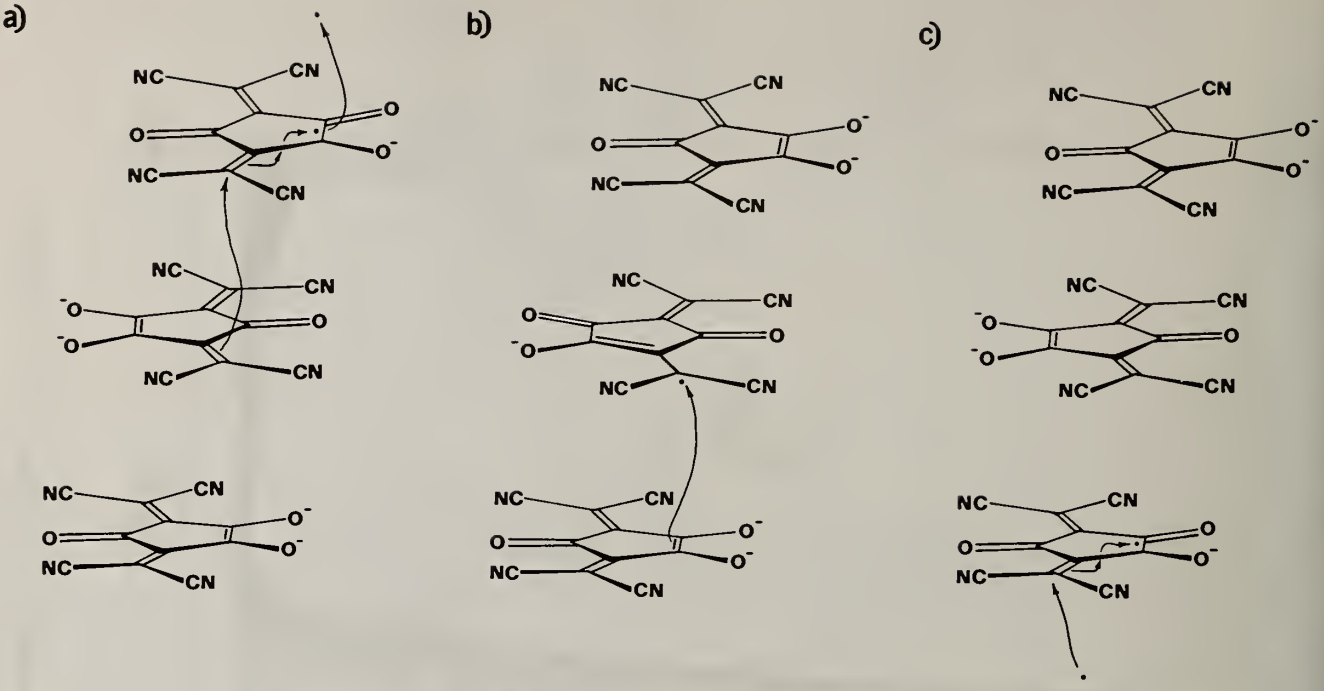


Figure 26. Views of three stacked croconate violet dianions showing proposed: (a) initial electron abstraction and intermolecular electron conduction between dicyanomethylene groups, (b) intermolecular electron conduction between the alkene carbon atom and the dicyanomethylene group (shown as resonance form here), and (c) intramolecular electron conduction between the alkene carbon atom and dicyanomethylene group.

9. A Multipurpose Cell for Nonaqueous Electrochemistry

Because the electrochemistry of many compounds involves radicals or water-sensitive moieties, the use of nonaqueous solvents is becoming increasingly popular. However, a not-so-trivial problem is obtaining solvents that are free of oxygen and water. Vacuum distillation and/or application of molecular sieves is generally sufficient to rid the solvent of water and organic impurities. Commonly, several vacuum freeze-pump-thaw cycles are employed to purge the solvent of oxygen. However, if the electrochemical experiment is not maintained under an inert atmosphere, such rigorous purification procedures are easily defeated.

We have designed and constructed a vacuum electrochemical system that easily maintains an oxygen- and water-free environment. The system employs an electrochemical cell usable in all types of electrochemical experiments (except polarography) and in some new applications, e.g., thin-layer electrochemistry and spectroelectrochemistry. The vacuum cell functions equally well in either of two configurations, i.e., as a spectroscopic cell in experiments employing an optically transparent thin-layer electrode (OTTLE) (figure 27A) and as an electrochemical cell in voltammetric experiments (figure 27B). The cell (in either configuration)

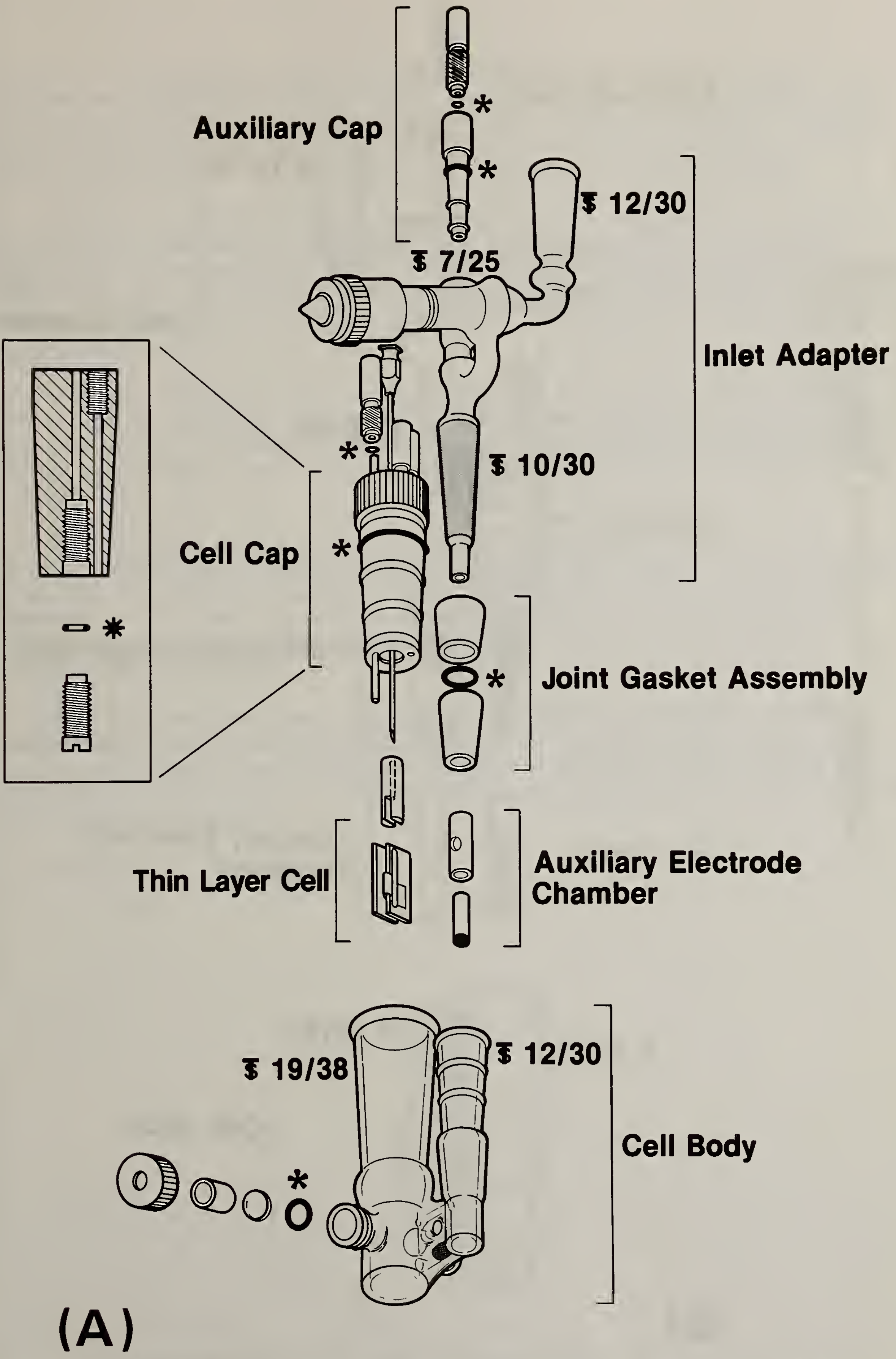
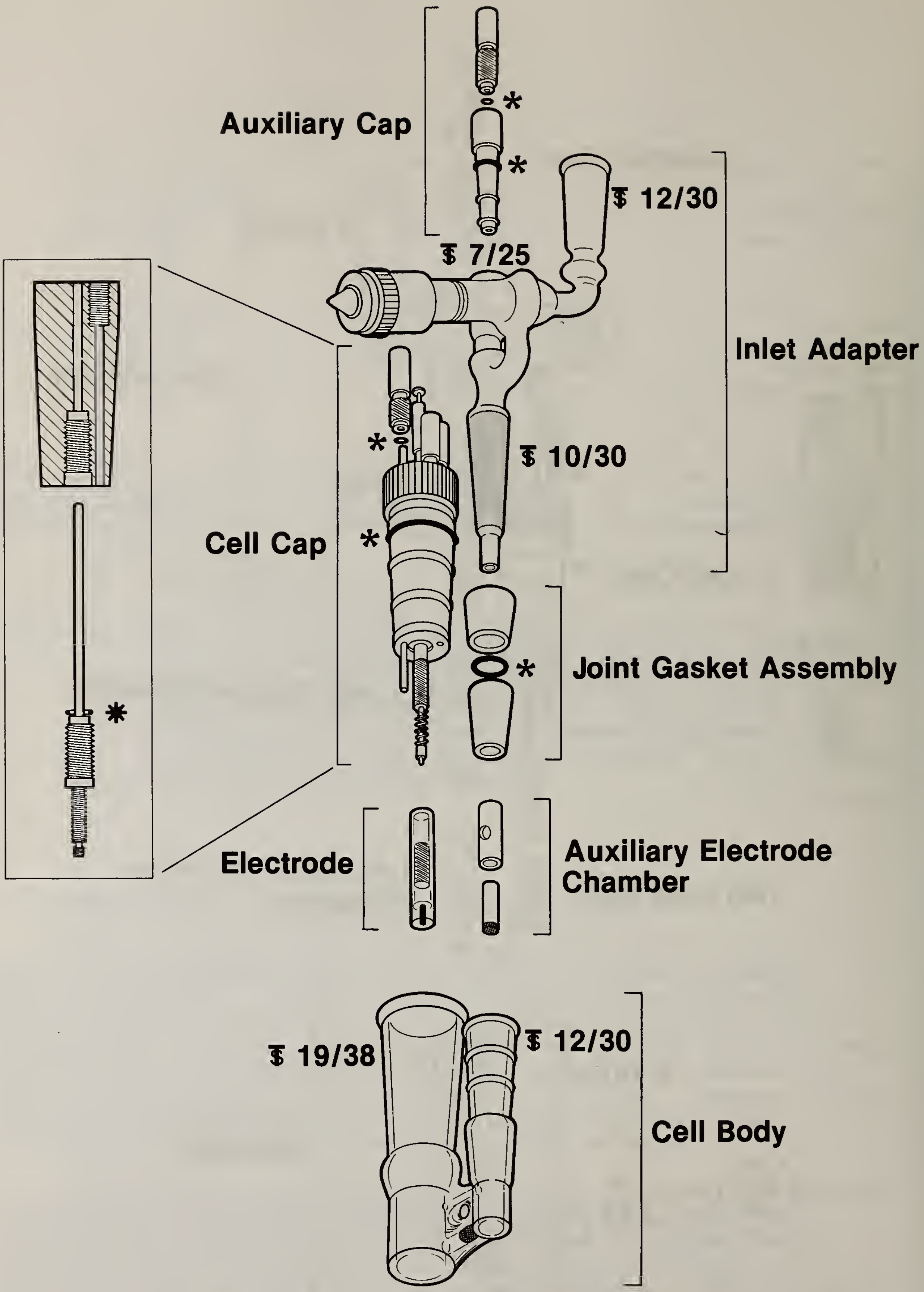


Figure 27A. Vacuum electrochemical cell: spectroelectrochemical apparatus. The asterisk indicates an O-ring.



(B)

Figure 27B. Vacuum electrochemical cell: bulk electrochemical apparatus. The asterisk indicates an O-ring.

consists of two parts: (1) the main U-shaped cell, which contains the solution and provides support for the electrodes and optical windows, and (2) the inlet adapter, which in part forms an isolated auxiliary electrode compartment and a port for solution introduction. Approximately 2 mL of solution are required to adequately fill the cell for an experiment.

Since the system is closed and under an inert atmosphere, the need for continuous purging is eliminated and cell transportation is facile, especially for laboratories where the solution preparation facilities are remote from the instruments. In addition, the lack of continuous purging removes the possibility of trace impurities in the purging gas accumulating in the solution.

Although the joints are standard taper, O-rings are utilized between several joints to effect greaseless vacuum seals which will not seize. With some joints, a groove is ground in the inner joint to accomodate the O-ring; with other joints, a joint gasket assembly is employed as depicted in figure 27.

The many uses of the cell are accomplished with a versatile cell cap. The cell cap provides support for the working and reference electrodes and is rapidly and easily converted to the appropriate configuration of the experiment. A variety of working electrodes utilizing gold, platinum, silver, and pyrolytic carbon have been constructed to easily mount in the cell cap (see figure 27B).

This cell has been used successfully in both configurations in the electrochemistry of several organic and inorganic compounds dissolved in N,N-dimethylformamide and propylene carbonate; we have characterized the electrochemistry of several oxocarbon salts and demonstrated their reversible electrochromic behavior.

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10. Chronoamperometry at Unshielded and Collarless Disk Electrodes

In order to better understand the redox processes occurring at solid electrodes and apply them in electrochemical investigations, theories and models have been developed to describe the chronoamperometric diffusion processes. The diffusion coefficient D of electroactive compounds can be accurately determined from chronoamperometry using shielded disk electrodes to conform to the conditions of one-dimensional diffusion. For unshielded electrodes, the simple Cottrell equation no longer applies, and suggestions have been made to correct this by taking into consideration the edge effect, i.e., lateral diffusion. Recently, two groups have published results of numerical simulation for unshielded electrodes [1,2]. We have tried to apply these to the chronoamperometric data we obtained for $K_3Fe(CN)_6$.

The conventional procedure is to plot $i\sqrt{t}$ versus $\sqrt{t}$, where i denotes current and t denotes time. Our data and the two least squares regression calculations suggested by Heinze [1] and Lingane [3] are illustrated in figure 28: (a) the dashed line results from use of a linear equation suggested by Lingane [3], and (b) the solid line results from the use of the simulation results of Heinze [1]. In (a), D was determined from the intercept of the straight line on the ordinate axis at t = 0, while in (b) D was determined from a nonlinear regression analysis.

Alternatively, i is shown as a function of $1/\sqrt{t}$ in figure 29. The dashed curve is a least square polynomial fit to the experimental points. D can be estimated from the extrapolated value of i as time approaches infinity, i.e., $1/\sqrt{t} = 0$. The solid straight line is drawn through the points (x_1, i_1) and (x_2, i_2), as suggested by Sato *et al.* [2], where $x_1 = (3/\sqrt{t_2} + 1/\sqrt{t_1})/4$ and $x_2 = (3/\sqrt{t_1} + 1/\sqrt{t_2})/4$; and the range of time where data are used is $t_1 \leq t \leq t_2$. Then from the slope and the intercept of this line at $1/\sqrt{t} = 0$, D is determined by an iterative procedure based on the numerical simulation results of Sato *et al.* [2].

The values of D as determined by the various procedures are summarized in Table 18.

Table 18. Diffusion Coefficient Determined by Various Procedures.

	Procedure	$D \times 10^6$ cm^2/s
a)	$i\sqrt{t}$ vs $\sqrt{t}$, linear	7.68
b)	$i\sqrt{t}$ vs $\sqrt{t}$, using Heinze's results	7.88
c)	i vs $1/\sqrt{t}$, extrapolate to $1/\sqrt{t} = 0$	7.8
d)	i vs $1/\sqrt{t}$, using Sato's results	7.54

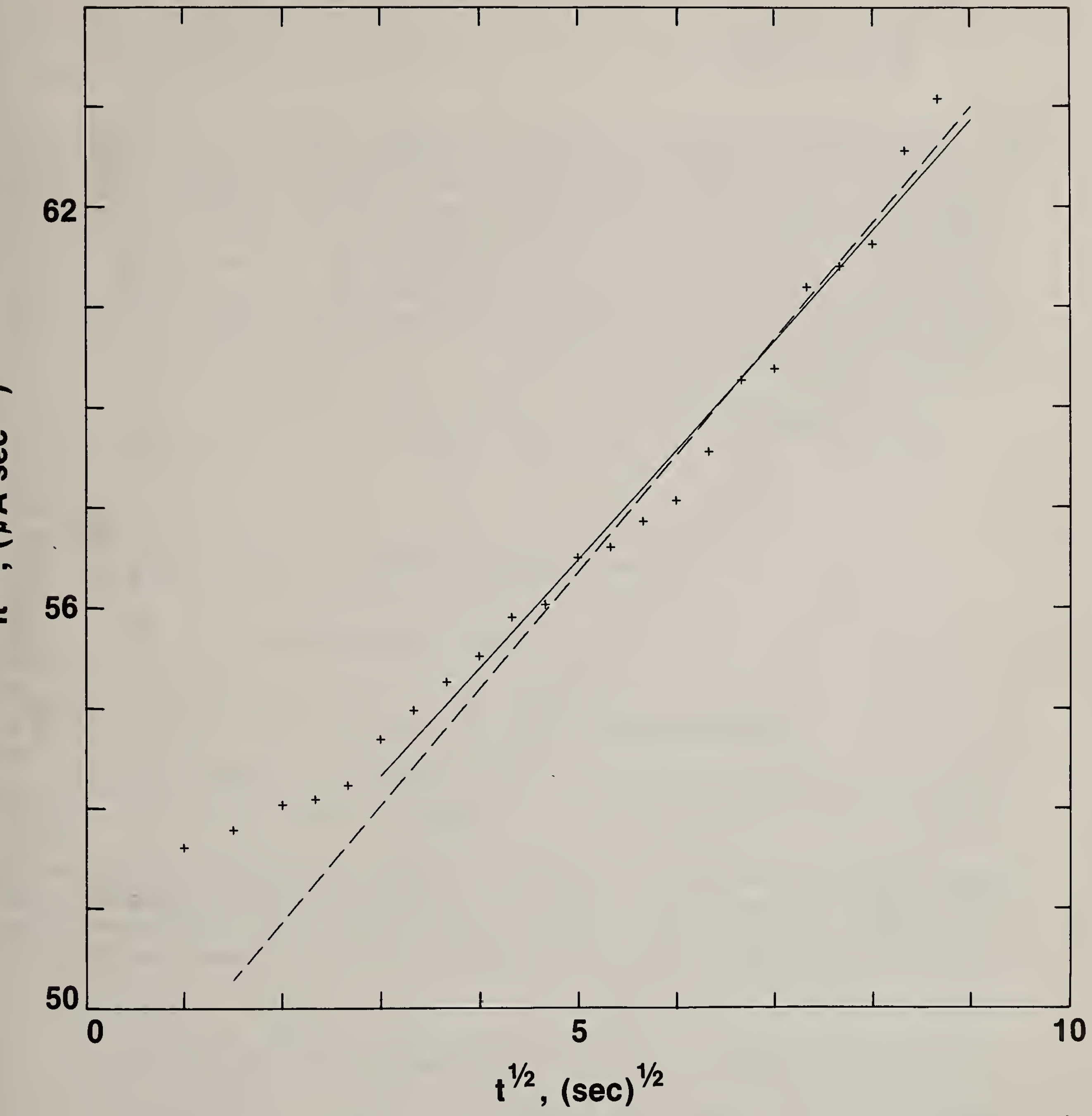

Figure 28. Plot of $i\sqrt{t}$ vs. $\sqrt{t}$.

The estimated percent deviation of each value is about ±5 percent and the values determined by the various procedures agree with each other within this limit of estimated deviation. The accepted value, reported by von Stackelberg *et al.* [4] is $D = 7.79 \times 10^{-6}$ cm^2/s. Procedures (a), (b), and (d) allow one to use the data at the middle range of current-time curves, thus avoiding the artifacts at an early time due to the electronics but also introducing some degree of arbitrariness in choosing the range.

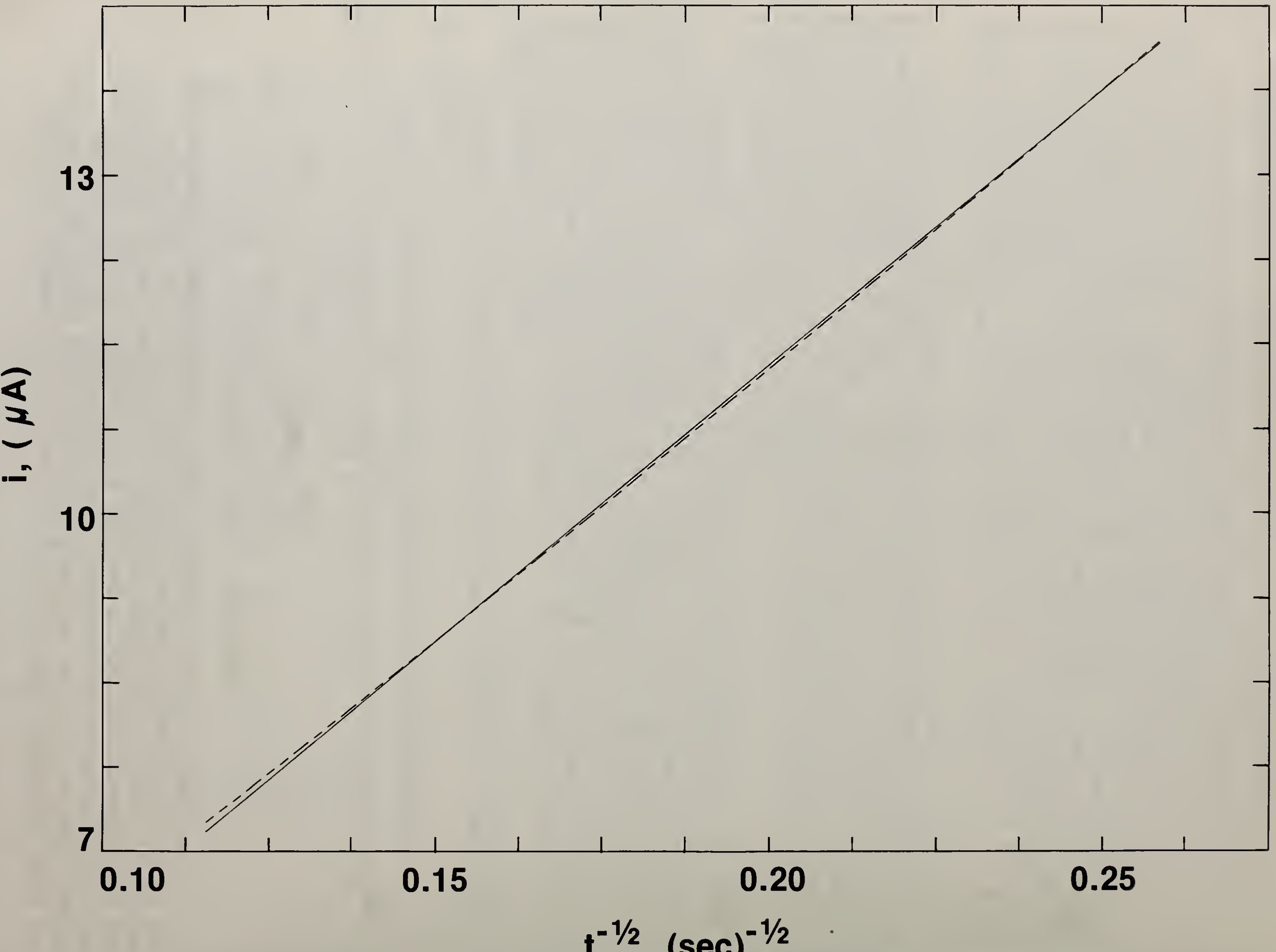

Figure 29. Plot of current versus $1/\sqrt{t}$.

Procedure (d) has appeal in that the two variables, i and t, are separate and their errors are not mixed as in the case of $i\sqrt{t}$, but this plot seems to be less sensitive as a diagnostic in our series of experiments as compared to the $i\sqrt{t}$ vs $\sqrt{t}$ plot.

Several articles have appeared recently, aimed at describing the current-time behavior in chronoamperometry employing unshielded disk electrodes, using both numerical simulation and analytical approximation. We have been developing a theory for chronoamperometry that is applicable to cylindrical rod electrodes insulated with a thin coating on the side, disk electrodes with a tapered collar, and several other electrode constructions which are easily fabricated. Solving the diffusion equation with the condition that the potential step is such that the concentration, C, of one of the species is zero on the disk, the current, i, as a function of time, t, is given by:

$$\chi(\tau) = \frac{1}{\sqrt{\pi t}} \int_{0}^{\infty} e^{-tz^2} \frac{\sin z\, J_1(z)}{z^2}\, dz + \int_{0}^{\infty} \mathrm{erf}(\sqrt{t}z) \frac{\sin z\, J_1(z)}{z}\, dz$$

where

$\chi \equiv \frac{i\pi a}{4nFAC}$ is the dimensionless current, and

$\tau \equiv \frac{Dt}{a}$ is the dimensionless time;

a is the radius of the disk and D the diffusion coefficient.

As $t \to o$ (small t or large a), the first integral dominates and $\chi(\tau) \to \frac{\sqrt{\pi}}{4} \frac{1}{\sqrt{t}}$, which is the Cottrell equation. On the other hand, as $t \to \infty$, the second integral dominates and $\chi(\tau) \to 1$, which is the behavior of the spherical electrode, as one would expect. The two integrals were evaluated by a series expansion of the Bessel function $J_1(z)$. The asymptotic expansion in fractional power of t at small t are still being investigated.

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L. M. Doane, W. T. Yap

11. Spectroelectrochemical Research: Surface-Enhanced Raman Spectroscopy of Pyridine Derivatives

Surface-enhanced Raman spectroscopy (SERS) is a recently discovered phenomenon which gives highly resolved spectral data of some molecular adsorbates. SERS is a currently unexplained phenomenon which produces a 10^6 enhancement of the Raman spectra of molecules adsorbed on metals such as silver and gold. Some of the theories which have been proposed involve coupling into surface plasmons via atomic, molecular, or large-scale surface roughness as well as field and image enhancement due to surface roughness.

The experimental apparatus can range from simple to elaborate. A simple system consists of general purpose Raman equipment--an argon ion laser, a double grating monochromator with a photomultiplier and photon-counting electronics with microcomputer-controlled data acquisition, storage, and display. A more elaborate system which could be used to monitor a broader range of compounds and surface reactions would consist of a tunable dye laser and multichannel detection. Several electrochemical cells have been designed consisting of a working electrode, counter electrode, reference electrode, and a port for deaerating the solution. A thin-layer cell has been designed to minimize the interference of solution spectra and to facilitate equilibrium of the redox reactions.

The enhancement of the spectra of surface species makes SERS an ideally suited technique for studying molecule-electrode interactions *in situ*. This technique has been successfully applied to studies of a number of pyridine derivatives (carboxaldehydes, methylketones, and carbinols) and the effects of adsorbate-substrate interactions have been identified. The 4-substituted carboxaldehydes and methylketones exhibit weaker carbonyl stretching bands when adsorbed on silver than in solution, while no such effect is found for the corresponding 3-substituted compounds. This is consistent with an interaction of the nitrogen lone-pair electrons with the silver, leading to electron withdrawal from 4-substituents and increased hydration of carbonyl groups at that position. Examination of several N-methylpyridinium salts shows a similar trend, with N-methylation increasing the degree of hydration and reducing the carbonyl band intensity in 4-pyridinecarboxaldehyde but not in 3-pyridinecarboxaldehyde. The effect of adsorption is more dramatic, however, since the SERS spectrum of 4-pyridinecarboxaldehyde is identical to that of the corresponding carbinol, indicating that the aldehyde is completely hydrated on the electrode. Thus, SERS allows us to identify the surface species and to show that it is quite different from that found in bulk solution. This result could not have been anticipated on the basis of cyclic voltammetry since no electrochemical reaction is required to produce the surface species.

Another study which has important implications on the surface metal interface uses N-methylpyridinium ions which only show surface enhancement when iodide is in the solution. No enchancement is observed with only chloride in solution and the effect of perchlorate is currently being investigated. These studies are important because the N-methylpyridinium ion has no nitrogen lone-pair electrons for bonding and is, in fact, an organic cation. These types of molecules have received little attention in SERS studies.

Many biomolecules undergo very slow heterogeneous electron transfer. This behavior is attributable to adsorption of the biocomponent on the electrode surface and/or isolation of the electroactive center by the protein matrix. This problem can be circumvented by addition of another species to the solution, a mediator-titrant, which transports electrons between the electrode and biocomponent. 4,4'-Bipyridine has been found to mediate electron transfer between cytochrome C and gold electrodes. Some workers have proposed that it mediates only when it is in a particular orientation with respect to the electrode surface. Preliminary results have indicated that this is not true on silver. SERS should be able to provide other valuable information on the interaction not only between the electrode surface and the mediator, but also the mediator and the protein.

It is anticipated that SERS will prove to be extremely useful in studying the surface characteristics of electrodes modified by the attachment of polymers and other electrocatalytic moieties. These polymer-modified electrodes are currently being investigated in our group to determine their properties and analytical potential.

K. A. Bunding, R. A. Durst

12. Measurements of the Optical Rotatory Dispersion of Internationally Exchanged Quartz Control Plates and Long Quartz Rotators Between 400 and 650 nm

Quartz control plates and rotators are used by national laboratories to assure comparability of measurements on their reference polarimeters. Several plates and rotators were exchanged between NBS and the Physikalisch-Technische Bundesanstalt (PTB) prior to determining a revised international value for the 100 °S point of sugar, a value that determines the market value of sugar. The developing use of lasers as light sources in polarimetric measurements also necessitated a study of the dependence of the optical rotation of these rotators at laser wavelengths before they be adopted as new polarimetric standard wavelengths.

Therefore, the optical rotatory dispersion of two long quartz rotators (∿15 mm long, supplied by PTB) and an NBS quartz control plate (∿1.5 mm in length) have been measured in the NBS high precision polarimeter at nine wavelengths between 400 and 650 nm using a Hg lamp and stabilized He-Cd, Ar, and He-Ne gas lasers. The rotation values along with their corresponding wavelengths were fitted to a four-parameter equation to calculate the following constants:

$$\frac{\alpha_\lambda}{\alpha_{633}} = -0.03955458 + 0.3673044985\ (\lambda-0.07359803)^{-1.79093432}$$

where α_λ = optical rotation at wavelength λ

α_{633} = optical rotation at 632.9914 nm (He-Ne laser source)

λ = wavelength in μm

Comparison of these data with Bünnagel's earlier measurements (1966) using lamp sources at the PTB on a 50 mm quartz rotator indicate that all four rotators, though of different origin, have a common rotatory dispersion (see Table 19). The fit of all four data sets to the Mandel four-parameter equation is excellent with reproduction of $\alpha_\lambda/\alpha_{633}$ to within 0.00002. This equation replaces the currently used seven-parameter equation derived from the fit of the single data set of Bünnagel. Hence, we have a firm corroborated formula by which optical rotation measurements at 633 nm performed with a stable, reproducible, inexpensive He-Ne laser source can be converted to corresponding optical rotator values at the 546 and 589 nm reference wavelengths for saccharimeters. Since certification at these wavelengths is a necessary part of our calibration service, measurement at this single wavelength has significantly shortened the time required for quartz plate calibrations by 25 percent. With user-submitted quartz control plates numbering over 70 during the last four years, the time savings is significant. The formula also provides a means by which the center of gravity wavelength of a spectral line can be determined to within a few ppm by measurement of its rotation by quartz rotators.

Table 19. Relative Optical Rotations of Internationally Exchanged Rotators Measured with Laser Sources.

Source	λ, nm	15 mm Rotator PTB #2 $\frac{\alpha_\lambda}{\alpha_{632.9914}}$	15 mm Rotator PTB #3 $\frac{\alpha_\lambda}{\alpha_{632.9914}}$	1.5 mm Rotator NBS #1724 $\frac{\alpha_\lambda}{\alpha_{632.9914}}$	50 mm Rotator Bünnagel Data Interpolated to our λ $\frac{\alpha_\lambda}{\alpha_{632.9914}}$
He-Cd	441.689	2.16015	2.16014	2.16023	2.16018
Ar	458.0630	1.99527	1.99525	1.99521	1.99523
Ar	476.6194	1.83055	1.83055	1.83050	1.83050
Ar	488.1225	1.73860	1.73861	1.73862	1.73858
Ar	496.6462	1.67495	1.67497	1.67494	1.67493
Ar	501.8559	1.63778	1.63777	1.63773	1.63775
Ar	514.6742	1.55148	1.55147	1.55143	1.55146
Hg Lamp	546.2271	1.36627	1.36629	1.36626	1.36628
He-Ne	632.9914	1.00000	1.00000	1.00000	1.00001

A. C. Cummings, D. K. Hancock, J. Mandel

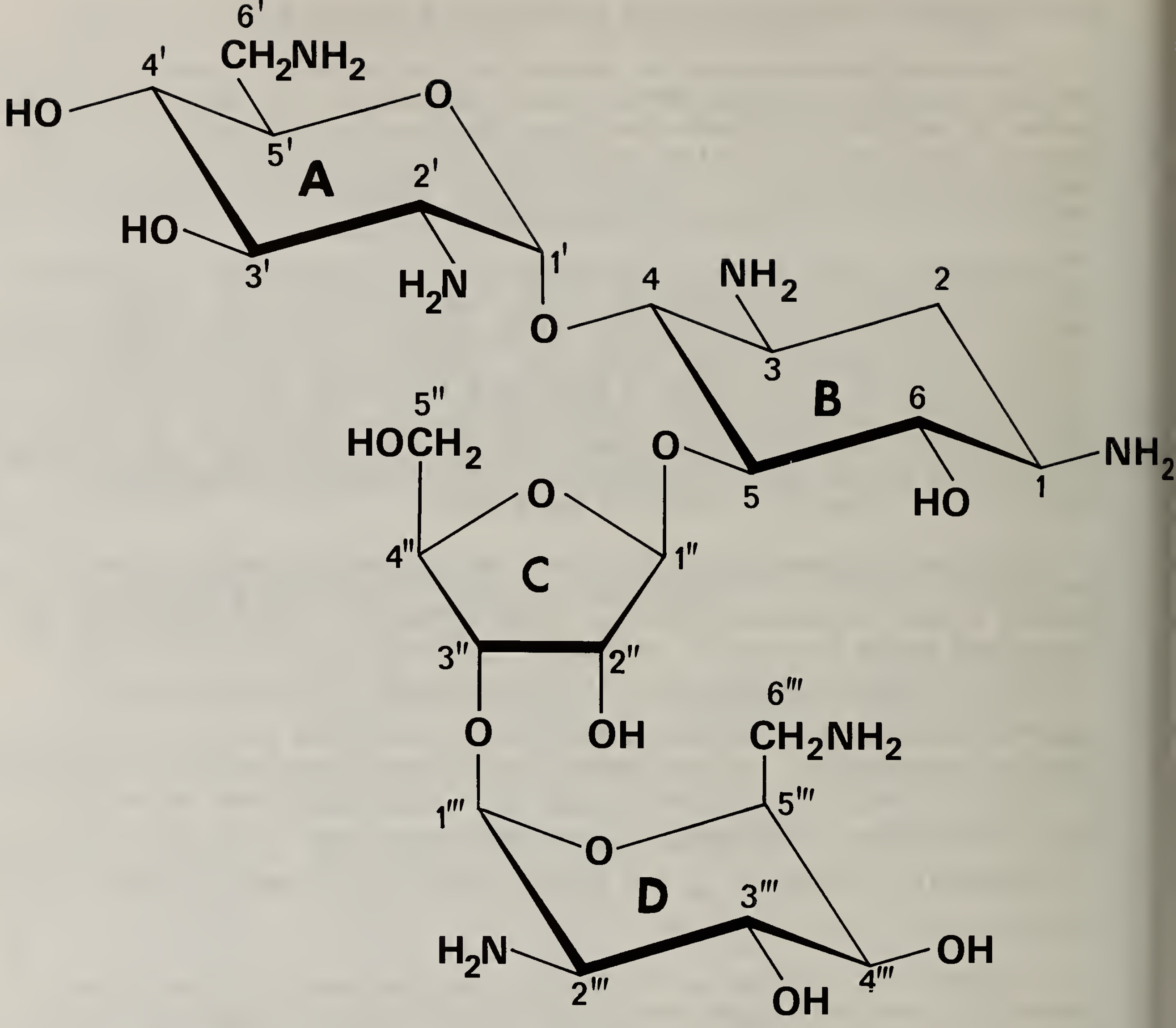
13. Nitrogen-15 NMR Spectroscopy of Neomycin B at High Field

The aminoglycoside class of antibiotics form a group of drugs that are of interest as possible future SRM's. Natural-abundance nitrogen-15 and 400 MHz proton NMR studies performed recently at the high-field NMR facility of the National Measurement Laboratory have demonstrated the usefulness of nitrogen and proton NMR parameters for the structural, conformational, and quantitative analysis of complex aminoglycoside molecules.

More than thirty years of considerable effort devoted to the isolation and characterization of components of the commonly prescribed "neomycin complex" has led to the elucidation of the structures of isomeric neomycins B and C in total stereochemical detail [1]. Despite this effort, however, the complete solution conformation of neomycin B (Structure 1) has not been defined with certainty. Results have been obtained, which, for the first time, describe conclusively conformational forms of individual sugar residues in Structure 1, and also illustrate the use of ^{15}N NMR for detection of impurities in commercial samples of antibiotics.

Nitrogen-15 chemical shifts of four derivatives of neomycin B are presented in Table 20 for comparison with the ^{15}N shift data of structurally related pseudo- and mono-saccharides shown in Table 21. Assignments of the resonances in the spectrum of the hexahydrochloride 1c are based on the ^{15}N shifts of hydrochloride salts of the components 2-7, except for the specific assignments of N-1 and N-3 which have been made on the basis of spin-labeling experiments. Similar chemical shift comparisons were used to classify nitrogens in the sulfate derivative 1a, the free base 1b, and the hexa-*N*-acetyl derivative 1d according to their structural type. Specific assignments of individual nitrogens in 1a and 1b were based on data obtained from ^{15}N chemical shift titration curves.

Complete ^{15}N chemical shift titration data for neomycin B are shown in figure 30. The complex behavior of the ^{15}N shifts with changes in pH is apparent, especially at intermediate pH values, where problems with peak overlapping and relative order of resonances are most severe. Once resonance assignments have been confirmed at the low pH extremes by comparing ^{15}N shifts of a sample of neomycin B hexahydrochloride (1c), the construction of smooth sigmoid curves through the points for individual nitrogens facilitates their assignment over the entire pH range. Chemical shift values extracted from the curves at pH 6.7 (indicated by the arrow) are within ±0.1 ppm of those determined for a solution of the sulfate 1a at the same pH. It is seen that protonation of the free base 1b leads to downfield shifts ranging from 6.8 to 14.2 ppm. It is also apparent from the titration curves that all of the amino groups in the antibiotic are essentially fully protonated at pH <4.5, and fully unprotonated at pH >10.5. The pK_a values for individual nitrogens shown in Table 22 were calculated from the titration curves.



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In general, the ^{15}N shifts of the N-acetylated compounds studied are 99.0-103.4 ppm downfield of the corresponding shifts of their free bases.

The close correspondence of ^{15}N shifts for nitrogens of a specific structural type in compounds which differ widely in their complexity, i.e., number of sugar units, indicates that substituents removed from the local environment (more remote than the γ-position) of the nitrogens have little influence on their chemical shifts. The small variations observed, however, may result from changes in solvation at the nitrogen sites with increasing complexity of the aminoglycoside. The substituent effect parameters derived for the aminoglycosides studied have been found to be in excellent agreement with those derived for simple aliphatic amino compounds [2]. Empirical methods have been developed to calculate nitrogen chemical shifts for aminoglycosides by using the substituent parameters.

Table 20. Nitrogen-15 Chemical Shifts of Neomycin B Derivatives in H_2O.

Derivative	Chemical Shift[a] N-1	N-3	N-2'	N-6'	N-2'''	N-6'''
Sulfate[b] (1a)	-340.4	-338.6	-343.4	-350.0	-347.8	-349.6
Free Base (1b)	-343.5	-345.8	-353.9	-361.8	-360.7	-359.8
Hexahydrochloride (1c)	-336.3	-337.9	-342.1	-349.3	-346.5	-348.9
Hexa-N-acetyl (1d)	-244.5	-246.3	-253.4	-259.8	-257.3	-257.7

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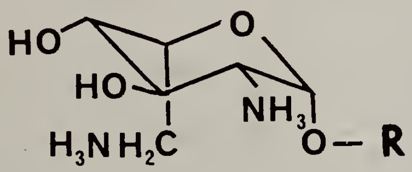
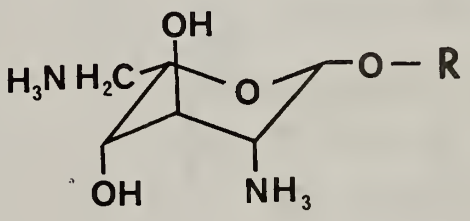
[a] In ppm upfield from an external capillary of 1M $NH_4{}^{15}NO_3$ in H_2O; negative values denote upfield shifts.

[b] pH = 6.7 of commercial preparation purchased from Sigma Chemical Co.

Based on the substituent effect parameters, N-2''' shifts calculated for L-idopyranosides in the $^4C_1$ conformation (Structure 2a) should be similar to those for 2-amino groups in D-glucopyranosides, but, in fact, the experimental values are consistently 4-6 ppm to higher field. Furthermore, earlier studies [3] have shown that the ^{15}N shifts of α-D-mannosamine derivatives, the structures of which are analogous to Structure 2b, are upfield of their respective α-D-gluco derivatives by similar increments to those found here. The data suggest that L-idopyranosyl residues in 1a-d adopt the $_4C^1$ conformation (2b) in solution. Proton NMR studies confirm this conclusion.



2a



2b

The ^{15}N chemical shift titration curves afford a method for the simultaneous measurement of the pK_a values of all nitrogens in the molecule that is far superior to conventional acid-base titrations. This is of general interest for the analytical characterization of other classes of nitrogen-containing materials.

Table 21. Nitrogen-15 Chemical Shifts of the Neomycin B Family of Aminosaccharides.

Compound Derivative	Chemical Shift[a] N-1	 N-3	 N-2'	 N-6'	 N-2'''	 N-6'''
Neamine						
Free Base (2a)	-343.7	-345.2	-353.8	-361.1		
Tetrahydrochloride (2b)	-336.9	-338.0	-342.2	-349.8		
Tetra-N-acetyl (2c)	-244.3	-246.1	-253.1	-260.2		
Methylneobiosiminide						
Free Base (3a)					-359.8	-359.6
Dihydrochloride (3b)					-346.4	-349.3
Di-N-acetyl (3c)					-256.7	-257.6
2-Deoxystreptamine						
Free Base (4a)	-344.9	-344.9				
Dihydrochloride (4b)	-337.7	-337.7				
Dihydrobromide (4c)	-337.6	-337.6				
Di-N-acetyl (4d)	-245.7	-245.7				
2,6-Diamino-2,6-dideoxyglucose						
Dihydrochloride (5a)			α: -342.2	-349.3		
(α:β = 71:29)			β: -343.9	-349.1		
Free Base (5b)			α: -352.6	-361.2		
(α:β = 75:25)			β: -353.3	-361.5		
2-Amino-2-deoxyglucose						
Hydrochloride (6a)			α: -341.7			
			β: -343.2			
N-Acetyl (6b)			α: -253.6			
			β: -254.4			
6-Amino-6-deoxyglucose						
Hydrochloride (7a)				α: β: -349.6		
N-Acetyl (7b)				α: β: -258.6		

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[a] In ppm upfield from an external capillary of $1\underline{M}$ $NH_4{}^{15}NO_3$ in H_2O; negative values denote upfield shifts.

Table 22. pK_a Values of Individual Nitrogens in Neomycin B.

N-1[a]	N-3[a]	N-2'	N-6'	N-2'''	N-6'''
8.08 ± 0.01	5.58 ± 0.05	7.49 ± 0.01	8.61 ± 0.04	7.58 ± 0.01	8.83 ± 0.01

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[a] Assignments based on spin-labeling experiments.

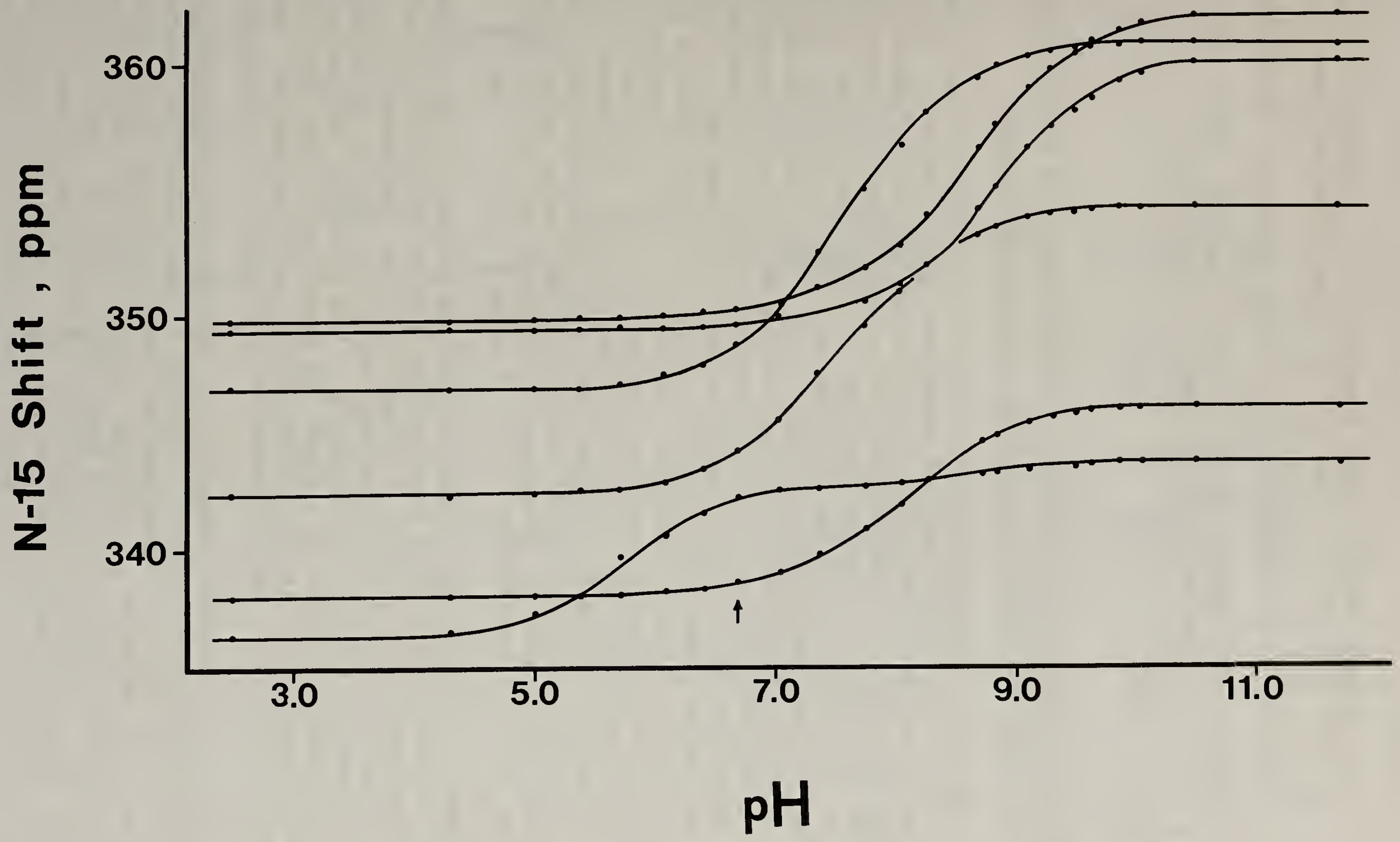

Figure 30. Nitrogen-15 chemical-shift titration curves for Neomycin B.

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R. E. Botto, B. Coxon

14. Nitrogen-15 NMR and Mass Spectral Characterization of Doubly ^{15}N-Labeled 2-Amino Oxazoline Derivatives of the Pentoses and Hexoses

The synthesis, characterization, analysis, and testing of anti-tumor nucleosides is an important facet of present-day cancer research. Because 2-amino oxazoline derivatives of carbohydrates can be used to prepare potential anti-tumor nucleosides (and nucleotides) in a single step, *via* three-carbon annulation reactions with various electrophiles, they would be very suitable for use in the preparation of radiolabeled anti-tumor nucleosides, especially those with isotopes possessing short half-lives. Such a class of radiopharmaceuticals based on pyrimidine cyclonucleosides is virtually unknown today and would have great clinical utility as nondestructive *in vivo* diagnostic imaging agents for use in nuclear medicine and clinical oncology. These short-lived radionuclides (^{18}F, ^{11}C, ^{13}N, ^{15}O) all decay by positron emission, and hence positron emission tomographic techniques (P.E.T.T. scanning) could be applied to them. Thus, a long-term goal of this work would be to provide a useful adjunct to the already well-established technique of isotope dilution mass spectrometry using stable isotope-labeled nucleoside anti-tumor agents in clinical settings. Carbohydrate derivatives of the 2-amino oxazoline type have previously been used in stereospecific syntheses of such anti-tumor nucleosides as 1-β-D-arabinofuranosyl cytosine (Ara C).

As part of a postdoctoral research associate project, a new efficient synthesis of doubly ^{15}N-labeled 2-amino oxazoline derivatives of carbohydrates has been developed which involves treatment of either unprotected or O-isopropylidene protected glycosylamines with cyanamide-$^{15}N_2$ in methanol to give glycofuranosyl 2-amino oxazolines-$^{15}N_2$. The structures and purity of many of these derivatives in the pentose and hexose series have been analyzed by proton, carbon-13, and nitrogen-15 NMR and by mass spectrometry. Reversed-phase HPLC proved to be a valuable means for purification of these compounds.

In figure 31, a probable mechanism for the formation of 2-amino oxazolines from glycosylamines and cyanamide in methanol at room temperature is presented. We postulate that the key intermediate for these labeled syntheses is an imonium ion which undergoes a transimination reaction with labeled cyanamide and then subsequent ring closures to give either furano or pyrano 2-amino oxazolines-$^{15}N_2$. Precedent for the invoking of an imonium ion was provided by the work of Frush and Isbell at NBS in 1951 [1]. These workers postulated an imonium ion intermediate in the mutarotation and hydrolysis of glycosylamines.

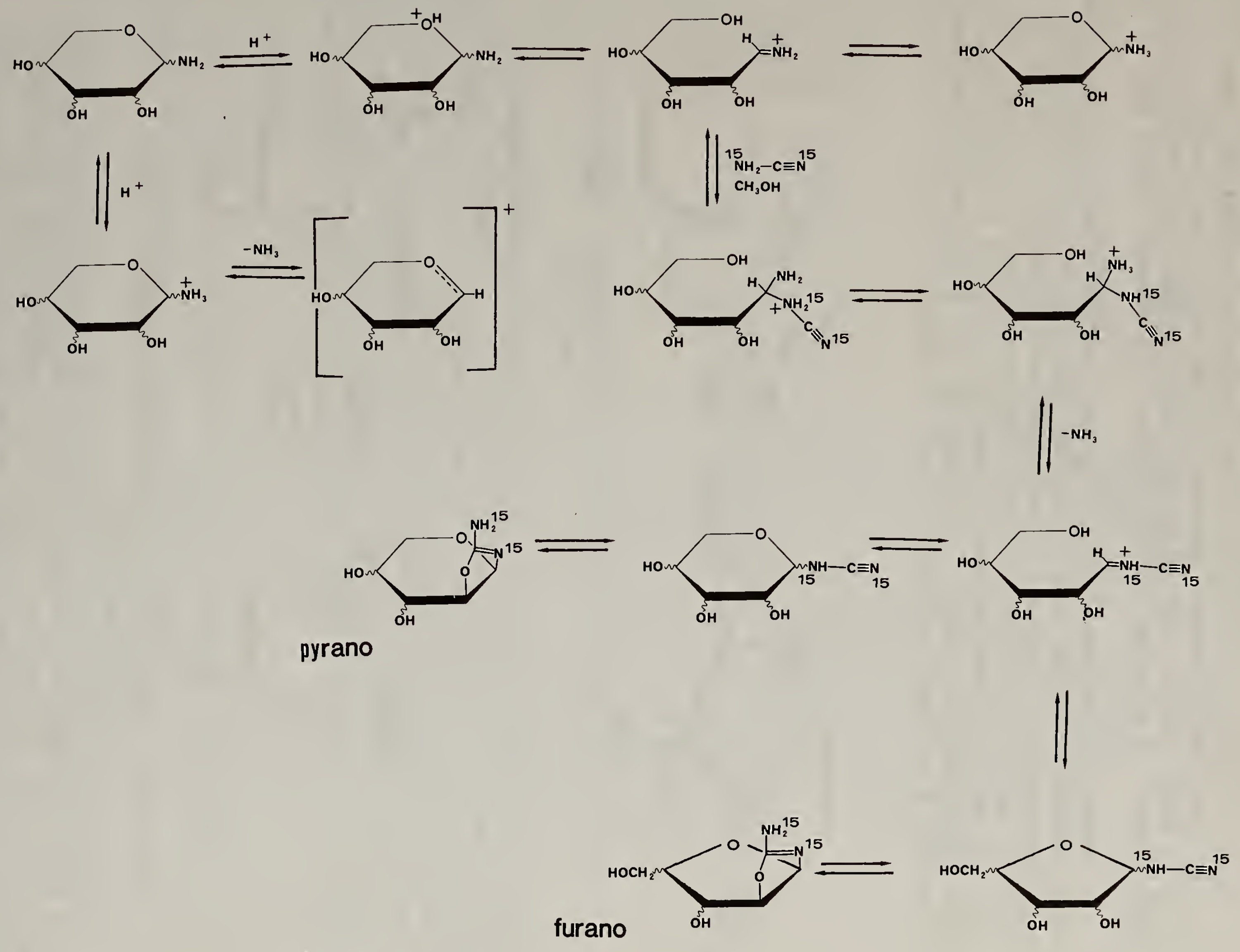


Figure 31. Probable mechanism for formation of 2-amino oxazolines from glycosylamines.

The inverted catenary (bell-shaped) pH *versus* log rate profile which they observed for glycosylamine hydrolysis explains in part how the glycosylamines are able to act as useful precursors of the 2-amino oxazolines. In the case of the ribose, arabinose, and xylose 2-amino oxazoline derivatives, only furano oxazolines were observed. However, in the case of the lyxose derivative, a 4 to 1 mixture of pyrano and furano 2-amino oxazolines is apparently formed, as detected by both TLC and C-18 reversed-phase HPLC.

In an attempt to prepare analytically pure samples of both lyxopyrano and lyxofurano 2-amino oxazolines and eventually also prepare them doubly ^{15}N-labeled, stereospecific syntheses of each form were undertaken. Figures 32 and 33 depict the stereospecific syntheses which have been worked out. In figure 32, the entire scheme has been successfully applied to arabinose and almost entirely to lyxose itself. In figure 33, the 5'-O-trityl lyxofurano 2-amino oxazoline has been isolated at about 75 percent purity.

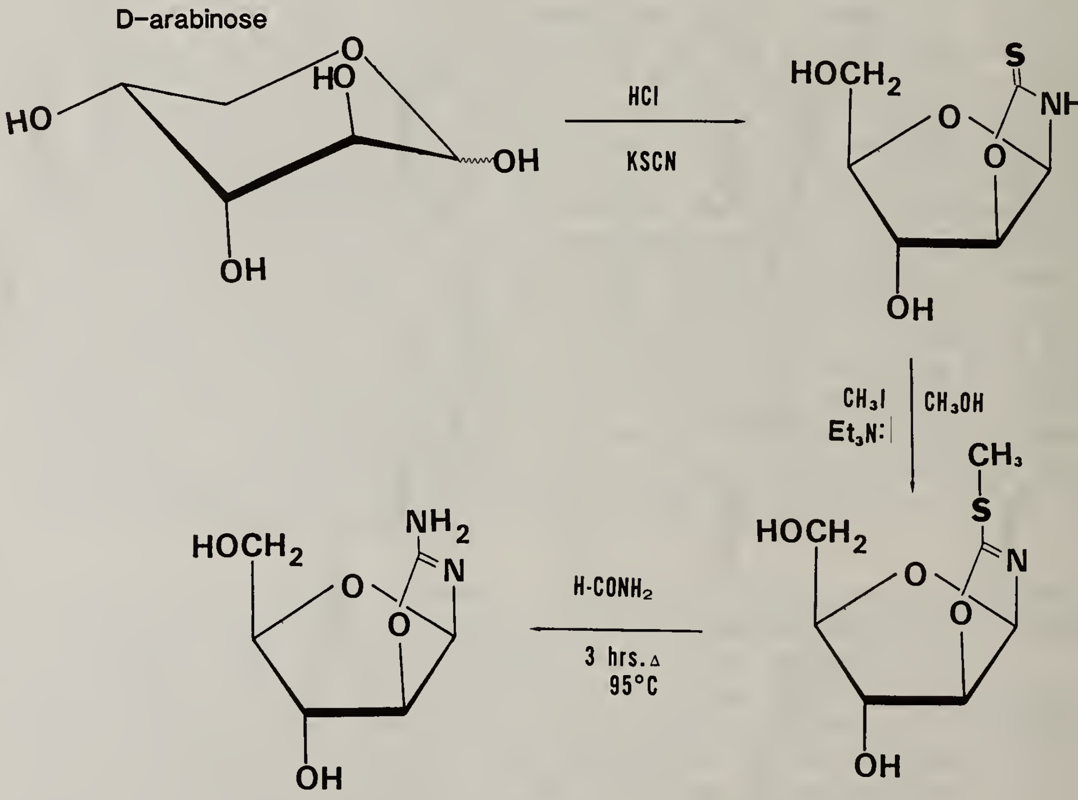


Figure 32. Stereospecific synthesis of arabinose furano 2-amino oxazoline.

In analyzing the structure and purity of one of the doubly ^{15}N-labeled 2-amino oxazolines, an interesting result was observed. The proton NMR spectrum of $^{15}N_2$-4,6-O-isopropylidene-2-amino-β-L-sorbofurano[2',3':4,5]2-oxazoline at 400 MHz in three different solvents displayed variations of vicinal ^{15}N coupling to H-1 and H-1', suggesting a dependence of proton dihedral angle on solvent.

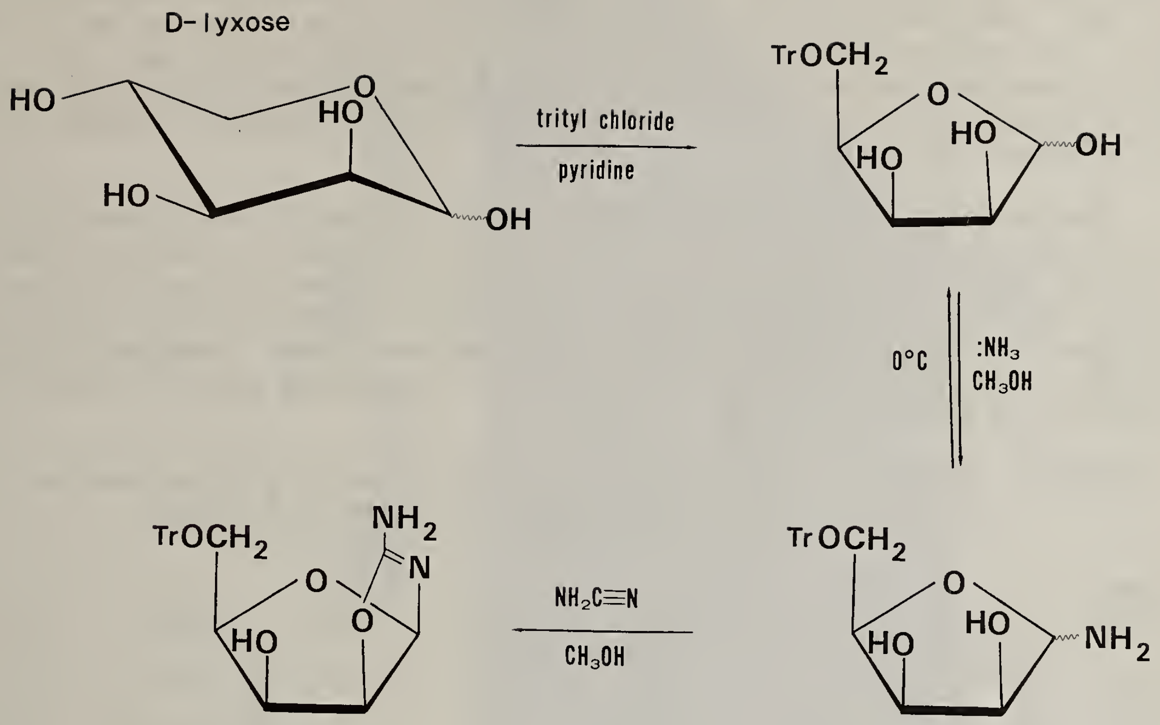


Figure 33. Stereospecific synthesis of lyxofurano 2-amino oxazoline.

These results suggest several experiments which are now being pursued. For example, since this ^{15}N-labeled sorbose derivative is apparently an ideal model system for distinguishing between intermolecular *versus* intramolecular H-bonding by use of ^{15}N NMR, it would be of theoretical value to correlate the temperature-dependent changes in the FT-IR of this compound in $CDCl_3$ or CD_2Cl_2 with the temperature-dependent changes in proton and ^{15}N NMR spectra at 400 MHz. Thus, an enthalpy value for an intramolecular H-bond in an aprotic solvent could be calculated from an Arrhenius plot.

Reference

[1] Isbell, H. S.; Frush, H. L. J. Res. NBS 46: 132; 1951.

B. Coxon, R. M. Davidson, S. A. Margolis, E. White V

15. Two-Dimensional Proton NMR Spectroscopy of Hydroxyl Proton Coupled α- and β-D-Glucopyranose

Solutions of α- and β-D-glucose in dimethylsulfoxide-d_6 (DMSO-d_6) are of interest as stable systems for the quantitative analysis of D-glucose (dextrose) SRM's by proton and carbon-13 NMR. However, inhibition of hydroxyl proton exchange in these solutions results in complex 12-proton spin systems that are difficult to interpret by conventional techniques. The proton NMR spectra of the major and minor components of SRM D-glucose (α-D-glucopyranose and β-D-glucopyranose, respectively) in DMSO-d_6 solutions have now been analyzed completely by application of the two-dimensional,'J'-resolved technique at 400 MHz. One great advantage of this technique is the separation of chemical shift and coupling constant information into different dimensions, which allows complex, overlapping proton signals to be disentangled by cross-sectioning methods, as long as there are at least slight differences in chemical shift between these signals.

The complete, two-dimensional proton NMR spectrum of β-D-glucose in DMSO-d_6 solution is shown in figure 34. Display of the 'J'-spectra cross-sections of the β anomer (see figure 35) permits the separation of all spin multiplets except the doublets due to HO-2 and HO-3, the chemical shifts of which are accidentally coincident under these conditions. Complete coupling constant data obtained by measurement of the 'J'-spectra cross-sections for both α and β anomers are shown in Table 23.

Table 23. Proton Coupling Constants (Hz) of α- and β-D-Glucopyranoses in DMSO-d_6 Solutions, Measured by 2-D NMR[a] at 400 MHz.

Anomer	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
α	3.6	9.7	8.7	9.7	2.3	5.0	11.2
β	7.7	8.9	8.5	9.4	2.2	5.9	11.8

Anomer	$J_{1,HO-1}$	$^4J_{2,HO-1}$	$J_{2,HO-2}$	$J_{3,HO-3}$	$J_{4,HO-4}$	$J_{6,HO-4}$	$J_{6',HO-6}$
α	4.8	1.2	6.6	4.8	5.4	5.2	6.4
β	6.6	0	4.7	4.8	4.9	5.5	6.3

---

[a] Data size: 8K x 128; Digital resolution in 'J' domain: 0.24 Hz/point.

These spectral analyses have been confirmed by other experiments in which simplified spectra were obtained for α- and β-D-glucopyranose by addition of one drop of trifluoroacetic acid to the DMSO-d_6 solutions. This procedure greatly increased the rate of hydroxyl proton exchange, and thereby removed the hydroxyl proton coupling constants from the CH proton spin multiplets. The addition of a catalytic quantity of trifluoroacetic acid also speeded anomerization, so that for additional confirmation of the spectral assignments of individual anomers by homonuclear spin decoupling, automated sequences of seven double-resonance experiments were performed, within 7-9 min after the addition of the acid, before significant anomerization had occurred.

The vicinal CH proton coupling constants (Table 23) indicate that α- and β-D-glucopyranose both adopt the $^4C_1$ chair conformation in DMSO-d_6 solution. Specific evidence for existence of the α-anomer in conformation (A), in which H-2, C-2, C-1, O-1, and HO-1 adopt a planar 'W'-arrangement, is afforded by observation of the unusual long-range coupling constant, $J_{2,\ HO-1}$ 1.2 Hz.

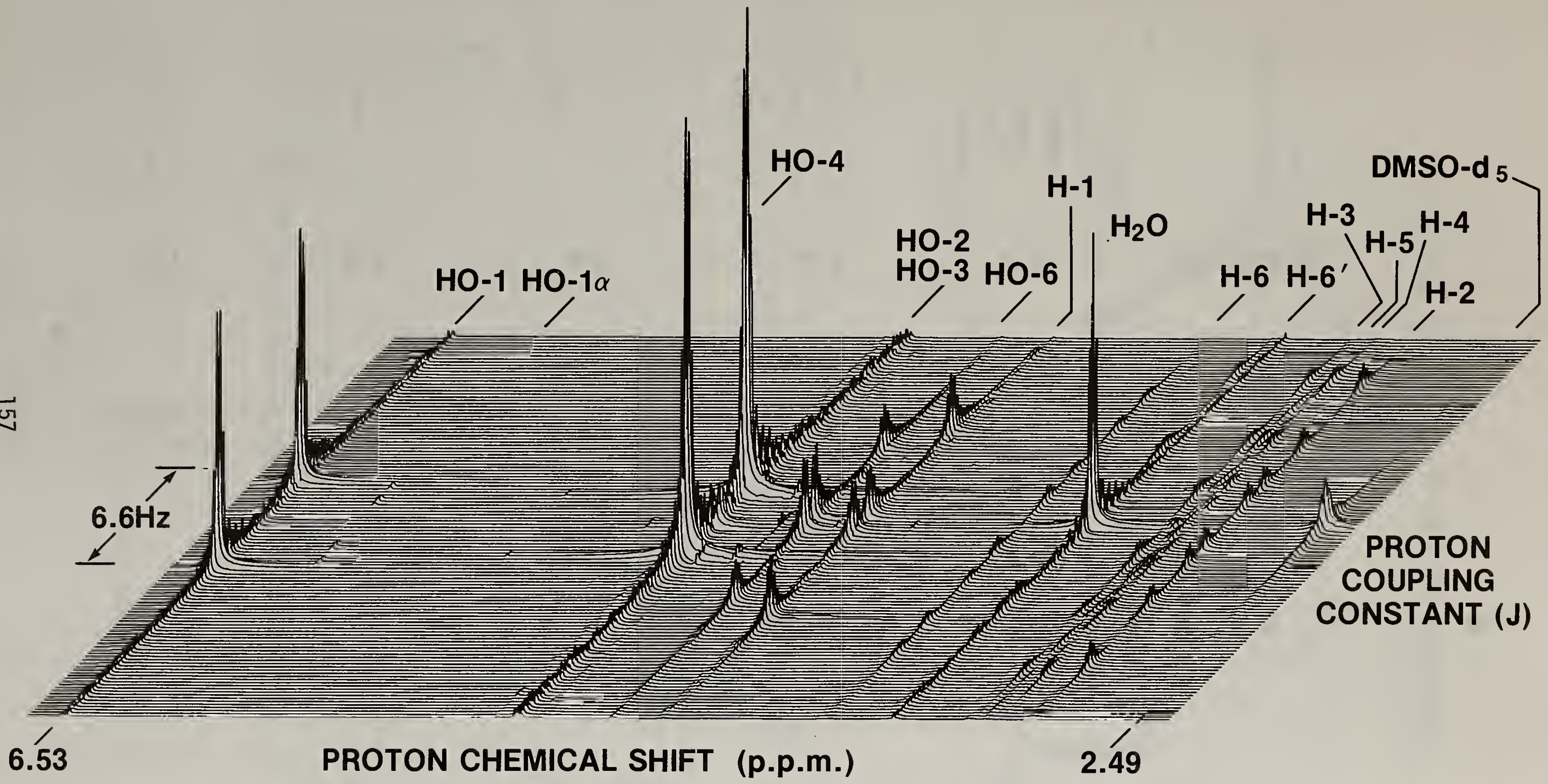


Figure 34. 2D J-resolved proton NMR spectrum of β-D-glucose in DMSO-d_6 at 400 MHz.

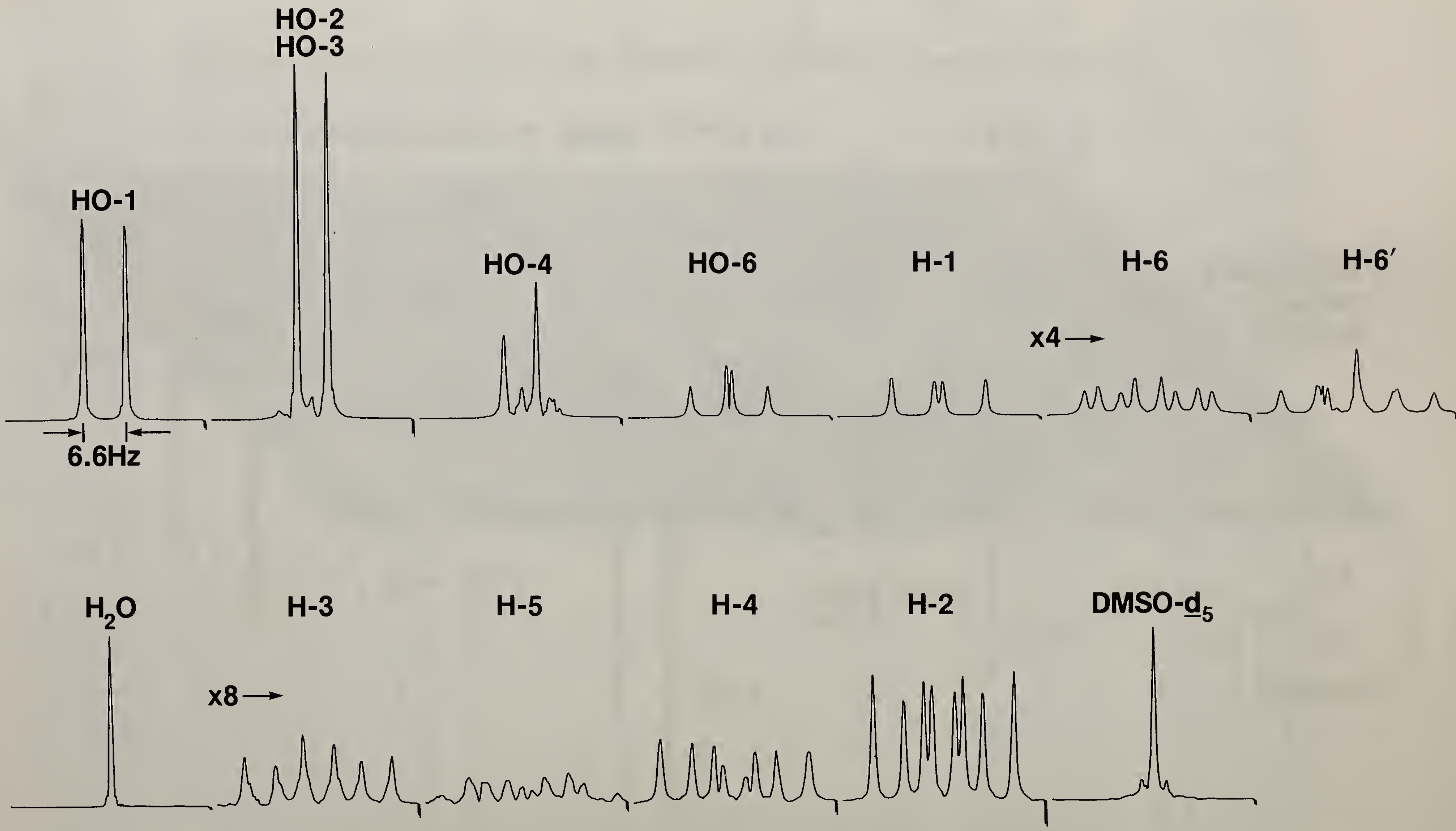
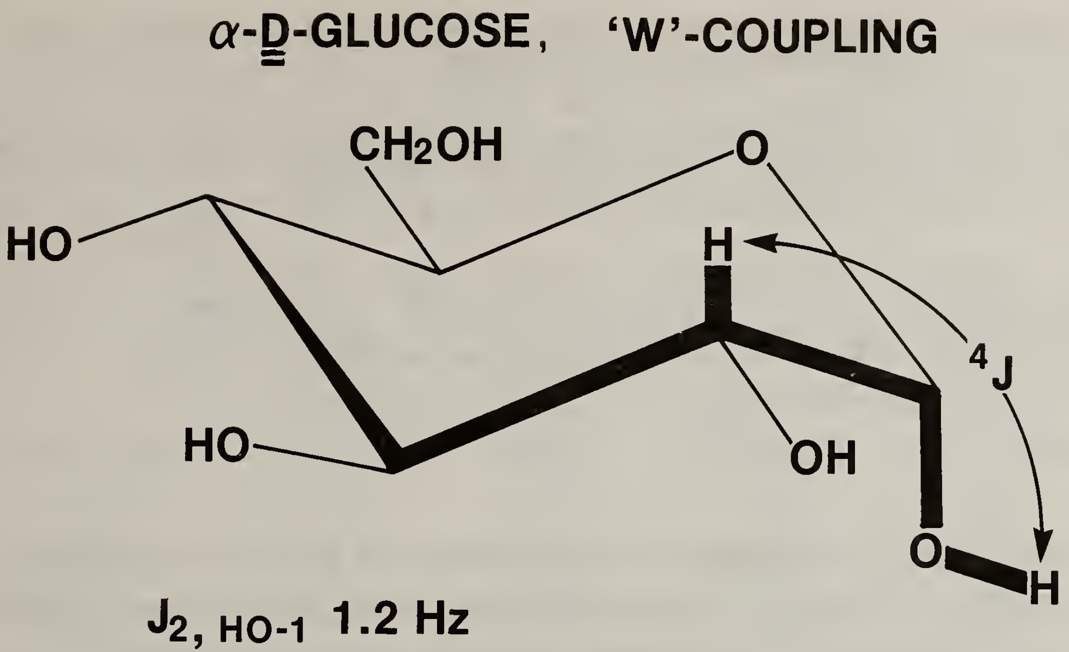


Figure 35. 2D NMR J-spectra at 400 MHz, β-D-glucose in DMSO-d_6, hydroxyl protons coupled.



(A)

This coupling constant is not observed for the β-anomer, and, in fact, the planar 'W'-arrangement is sterically impossible in this anomer. The favored orientation of HO-1 in the α-anomer may be attributed to steric crowding of HO-1 by DMSO-d_6 molecules hydrogen bonded to HO-2 and HO-3.

The efficiency of data acquisition for both one- and two-dimensional NMR depends on the proton spin-lattice relaxation times (T_1) of the sample, since the pulse sequence cannot normally be repeated at intervals of less than $5T_1$. Therefore, the proton T_1 values of α- and β-D-glucopyranose have been measured under the conditions used for the two-dimensional spectroscopy. The inversion-recovery method was used together with analysis of the data by means of an iterative, three-parameter exponential fit. The T_1 results are shown in Table 24. For solutions of the anomers in DMSO-d_6, the pyranoid ring protons show T_1 values in the range 0.5-0.7 s, the methylene protons values of 0.3 s, and the hydroxyl protons, 0.9-1.1 s. This interesting difference between ring (CH) protons and hydroxyl protons may be due to either greater mobility of the hydroxyl protons (shorter correlation time), or to association (by hydrogen bonding) of the hydroxyl protons with solvent molecules containing deuterium nuclei that are relatively poor relaxers of protons. Measurements of solutions of α- and β-D-glucose in non-deuterated dimethylsulfoxide are in progress, to test these hypotheses. However, the results indicate that the pulse sequence for two-dimensional NMR should not be repeated more often than once every 5.5 s.

Table 24. Proton Spin Lattice Relaxation Times (T_1, Sec) of α- and β-D-Glucopyranoses[a] at 400 MHz.

Anomer	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	HO-1	HO-2	HO-3	HO-4	HO-6
α	0.7	0.6	0.6	0.6	0.5	0.3	0.3	0.9	1.1	1.0	0.9	1.0
β	0.6	0.7	0.6	0.6	0.6	0.3	0.3	1.1	1.0	1.0	0.9	1.1

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[a] Concentration: 100 mg of α- or β-D-glucose in DMSO-d_6 (1.0 mL).

B. Coxon

16. Comparison of Two Isotope Dilution Definitive Methods for the Determination of Glucose in Serum and Evaluation of the American Association for Clinical Chemistry Candidate Reference Method for Glucose

The measurement of serum glucose levels is one of the most important and most commonly performed analyses in the clinical laboratory. Clinical chemists employ many different methods to determine serum glucose levels. When these methods are compared on serum pools, serious discrepancies are found in the results. Methods of demonstrated high accuracy and precision are needed to provide an accuracy base to which the clinical methods can be compared. The Centers for Disease Control undertook the development of a reference method with which clinical laboratories could evaluate their procedures. To establish the accuracy of the proposed reference method [a modified hexokinase/glucose-6-phosphate dehydrogenase (HK/G6PDH) procedure], the Standards Committee of the American Association for Clinical Chemistry asked NBS to develop an isotope dilution mass spectrometric (ID/MS) definitive method for serum glucose.

A brief description of the first ID/MS method for serum glucose developed at NBS is as follows: A known weight of uniformly labeled ^{13}C-glucose is added to a known weight of serum. After the serum is allowed to equilibrate, it is freeze-dried. The serum is then treated with acetone under anhydrous conditions to convert glucose into 1,2:5,6-di-O-isopropylidine-α-D-glucofuranose (DAG). Three thin-layer chromatography steps are employed to separate DAG from other reaction products including the acetone-condensation products with other hexoses. For the initial comparison of this method with the reference method, samples were introduced to the mass spectrometer via the direct insertion probe. All later work involved sample introduction via packed column gas chromatography. Measurements are made on a low resolution magnetic sector instrument operated in the electron impact (EI) mode. Magnetic switching is employed in the sequential monitoring of the $(M-15)^+$ ions for the labeled and unlabeled DAG. The measured unlabeled/labeled ratio from serum samples is compared with the measured ratios of calibration standards, which consist of known weights of SRM glucose and uniformly labeled ^{13}C-glucose, converted to DAG. For quantitation, each sample measurement is bracketed by measurements of the two calibration standards whose ratios most closely bracket that of the sample. Linear interpolation is then used to calculate the amount of glucose in the sample.

The results of the initial comparison of our ID/MS method with the HK/G6PDH reference method is summarized in Table 25. The reference method results are a composite of the results obtained from twelve laboratories, including NBS, on five serum pools analyzed in quadruplicate over a five-day period. The results demonstrate that the methods agree well for all pools tested. A full report of this study is undergoing review for publication as an NBS 260 report.

Table 25. Comparison of Candidate Reference Method Results with ID/MS Target Values. Differences and Standard Deviations in mg/L.

	Manual[a] - ID/MS		Semi-Automated[b] - ID/MS	
Pool Mean	Difference	S.E.D.[c]	Difference	S.E.D.[c]
409.0	4.4	4.5	8.9	2.9
785.8	7.6	5.5	4.1	4.0
1344.4	- 1.1	7.3	- 3.0	6.3
1969.7	-19.2	9.8	-32.2	9.0
2978.7	-36.9	13.9	-48.6	13.6

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[a] Candidate reference method with manual pipetting.

[b] Candidate reference method with semi-automated pipetting.

[c] Standard error of the difference.

A second ID/MS method was devised to provide a much simpler wet chemical procedure as well as to verify the accuracy of the DAG method. This approach utilizes the same labeled glucose, but differs markedly otherwise. After equilibration, the serum is treated with ethanol to precipitate protein and the deproteinized serum is freeze-dried, treated with 1-butylboronic acid in anhydrous pyridine followed by acetic anhydride to form the derivative, α-D-glucofuranose cyclic 1,2:3,5-bis-(butylboronate)-6-acetate (glucose BBA). Separation of glucose BBA from the BBA derivatives of other monosaccharides is accomplished by gas chromatography using a 100 m SCOT capillary column. Measurements are made in the electron impact mode, using the $(M-57)^+$ ion, which is a prominent fragment ion for glucose BBA but only a minor fragment ion in the mass spectra of other hexose BBA's. Bracketing of the samples with similarly derivatized calibration standards is again used for quantitation. Table 26 shows the results for the comparison of the two ID/MS methods, performed at NBS, with the reference method, performed simultaneously at CDC, on three human serum pools.

Table 26. Comparison of the Two ID/MS Derivative Methods and the CDC Reference Method on Three Human Serum Pools Sampled Simultaneously. Mean Results are in mg Glucose/g Serum.

	DAG		Glucose BBA		HK/G6DH	
Pool	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)
A	0.6843	0.29	0.6779	0.19	0.6845	0.51
B	1.803	0.15	1.790	0.17	1.794	0.29
C	2.919	0.24	2.901	0.18	2.912	0.22

The agreement of all three methods is excellent (<1 percent range for each pool). To check for interferences, samples from each pool were remeasured under isobutane chemical ionization (CI) conditions, with monitoring of the $(M+1)^+$ ions for both DAG and glucose BBA samples. The CI results agreed with the EI results within the uncertainties of the measurements.

Our results have shown that both ID/MS methods are very precise, and after exhaustive testing, we have found no bias sufficient to interfere with the intended uses of either method. Therefore, each method satisfies the requirements for a definitive method. However, when the two are compared on identical serum samples, the DAG results are consistently higher than the glucose BBA results by a small but statistically significant amount (<1 percent for all pools tested). When compared on an aqueous glucose solution, the two methods agree within the uncertainties of the measurements. Therefore, the small systematic difference observed is related to the presence of the serum matrix. The two ID/MS methods have been described in a manuscript to be submitted to Biomedical Mass Spectrometry. The excellent agreement of the KH/G6PDH results with the ID/MS definitive method values proves that the CDC method fulfills the requirements of a reference method.

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

17. Comparison of Two Isotope Dilution/Mass Spectrometry (ID/MS) Methods for the Determination of Total Serum Cholesterol

Both U.S. and international societies for clinical chemistry recognize the need for definitive (i.e., essentially bias-free and highly precise) methods that can serve, along with high-purity SRM's, as the accuracy base for clinical chemistry. NBS has developed a candidate definitive method for total serum cholesterol involving ID/MS. Our publication [Clin. Chem. 26, 854-860 (1980)] provides data that show the absence of interferences in the ID/MS measurements involved in the method and the high reproducibility of the results, thus demonstrating the method's accuracy and precision. To ensure scientific validity, we sought external confirmation by comparison with another laboratory.

Researchers at the Karolinska Institute (KI), Stockholm, Sweden, who were the first to report an ID/MS method for total cholesterol [1], used their method to analyze samples of the same serum pools as were run at NBS. Their analyses gave results with mean values consistently lower than the NBS values for those pools. NBS study of the cholesterol used at the KI as primary standard revealed that it contained lathosterol, an isomer of cholesterol that interfered with the KI measurement method. When the KI reanalyzed the serum pools with SRM cholesterol used as the primary standard, the bias was no longer evident, with mean values for the pools ranging from 1.5 percent below to 1.5 percent above the NBS mean values (Table 27). The imprecision of the results obtained at the KI was about the same for the two series of analyses and were from three to ten times larger than the NBS values. Several aspects of the KI method have been identified as contributing to the imprecision. Although no systematic bias is now apparent between the two methods, the imprecision of the KI method limits its usefulness for confirming the accuracy

Table 27. Total Cholesterol Concentrations as the Mean ± One Standard Deviation of the Mean in mmol/L, for Five Serum Pools, as Determined by ID/MS in Two Series of Analyses at the Karolinska Institute (KI) and One at the National Bureau of Standards (NBS).

Laboratory	Pool					
	N[a]	A	B	C	D	E
KI/first[c] series	8	3.39 ± .058[b]	4.68 ± .036	6.11 ± .046	7.35 ± .054	8.59 ± .088
KI/second[d] series	8	3.39 ± .019	4.73 ± .059	6.15 ± .046	7.57 ± .112	8.85 ± .064
NBS	16	3.43 ± .006	4.72 ± .008	6.15 ± .011	7.47 ± .011	8.79 ± .015

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[a] N is the number of measurements per pool.

[b] Calculated from an analysis of variances [2].

[c] Analyses performed without SRM Cholesterol as the primary standard.

[d] Analyses performed with SRM Cholesterol as the primary standard.

of the NBS method as a definitive method. (The KI method was not designed to serve as a definitive method.) Conversely, the NBS method, which has been rigorously tested for accuracy in-house, does prove that the KI method fulfills the accuracy requirements of a reference method. The comparison of these ID/MS methods has been described in a manuscript submitted to Clinical Chemistry.

References

[1] I. Bjorkhem, R. Blomstrand, and L. Svensson, Clin. Chim. Acta 54, 185 (1974).

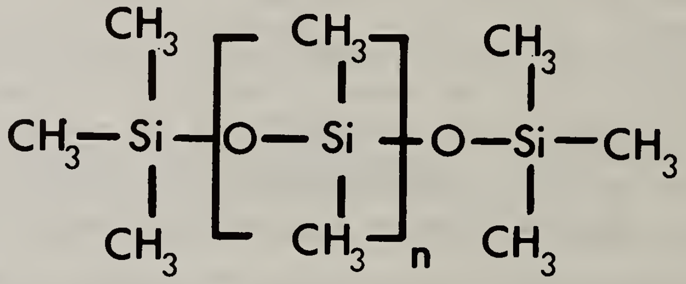
[2] J. Mandel and R. Paule, Anal. Chem. 42, 1194 (1970).

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

18. Identification of Components Leached from Implants Made of Siloxane Polymers and Influence on Prolyl Hydroxylase Activity

Use of a mammary prosthesis following radical mastectomy or for cosmetic purposes has become a common medical practice. However, after implantation these prostheses are frequently encapsulated with collagenous tissue to such an extent that the patient finds it necessary to have them removed. In current practice, mammary augmentation devices usually consist of an outer siloxane envelope filled with either a siloxane gel or siloxane gel-saline mixture. Our research for the Food and Drug Administration (FDA) was designed to determine whether there is a substance leaching from the implanted device which activates the enzyme system for collagen production. Researchers at FDA had evidence that gel may be diffused through the envelope.

Test samples of prosthesis envelope and gel were obtained from Dow Corning Corp. To ten-gram quantites of prosthesis gel in rigorously cleaned glass containers was added 20 mL of purified water. The mixture was stirred slowly for four hours, then the leachate-containing water was decanted into a 500 mL acid-cleaned flask, after which water was removed in a rotary evaporator. Water from ten leachings was pooled. Leachate residue was dissolved in 25 mL of 0.04 M TRIS-HCl (pH 7.6) buffer solution which was centrifuged to remove particulate matter. This leachate was used to study influence on enzyme activity. Alternatively, leachate-containing water was extracted with methylene chloride. The composition of the extract was determined by gas chromatography/mass spectrometry, and was found to consist largely of dimethylsiloxane fragments,



$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-\left[O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\right]_n-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_3}$$

for which n had values of 0-3.

Prolyl hydroxylase was chosen for the study of leachate influence on the collagen-forming enzyme system, because its activity is considered to be rate limiting. This enzyme was extracted from the leg bones of 15-day chick embryoes. Its substrate, protocollagen, was obtained from the calvaria of these embryoes incubated with gentle shaking for 24 hours in tissue culture with tritium-labeled proline at 37 °C. Enzymatic activity assay was performed by mixing enzyme, substrate, and cofactor solution, incubating at 37 °C for 15 min, then stopping the reaction with trichloroacetic acid. The mixture was centrifuged and tritiated water separated from other soluble tritiated compounds with a cation exchange resin. Enzyme activity is proportional to the amount of tritiated water found in this procedure. No rate influence on the prolyl hydroxylase by the silicone leachate was observed. Rate studies employing leachate from silicone envelopes similarly did not show measurable effects. Small quantities of ethyl alcohol, α,α'-dipyridyl, or dimethylsulfoxide, however, were shown to be inhibitory.

A. E. Davidson, S. N. Chesler, L. R. Hilpert, B. F. Howell, D. J. Reeder, E. White V

19. Combined LC/MS Techniques: Development of an Interface System Compatible with Reversed-Phase LC

High-performance liquid chromatography (HPLC) can be used for the separation of many nonvolatile and polar molecules that are not amenable to gas chromatography and can handle many samples in matrices that are difficult to analyze directly by gas chromatography, such as water or heavy oil. Therefore, the coupling of a mass spectrometer, a universal and/or selective detector, to a liquid chromatograph has generated a great deal of interest. Numerous publications have appeared and two methods have been used in commercial instrumentation.

Due to the limitations of existing interfaces, we have constructed a unique LC/MS interface that operates by removing most of the excess solvent from the effluent stream as it flows down a heated wire. The residual concentrated solution is drawn into the vacuum of the mass spectrometer and volatilized into the ion source. It has been found to perform satisfactorily with several normal-phase chromatographic separations. The interface and some applications are described in the previous annual report and in Christensen *et al.*, Anal. Chem., 53, 171 (1981).

A large portion of analytical LC is now performed using reversed-phase chromatography and it is, therefore, desirable to accomodate the aqueous solutions used in that chromatographic mode. The only part of our system which did not operate well with water was the probe which introduced the concentrated stream into the ion source. The difficulty arose because of the high surface tension and heat of vaporization of water. Attempts to overcome the problem by heating the tip of the probe were unsuccessful. A sonic spraying device was developed, using a solenoid coil around the exterior part of the solvent introduction capillary (see figure 36). The capillary, being made of nickel, is magnetostrictive, so that an alternating field causes it to vibrate. When tuned to resonance, the vibration is strong enough to cause 25 µm diameter water droplets to be sprayed from the surface at the tip of the probe. Concentrated buffer solutions can be sprayed without evaporative deposition clogging the 8-10 µm orifice; adenosine, a test compound of low volatility, can be dispersed well enough to observe a molecular ion.

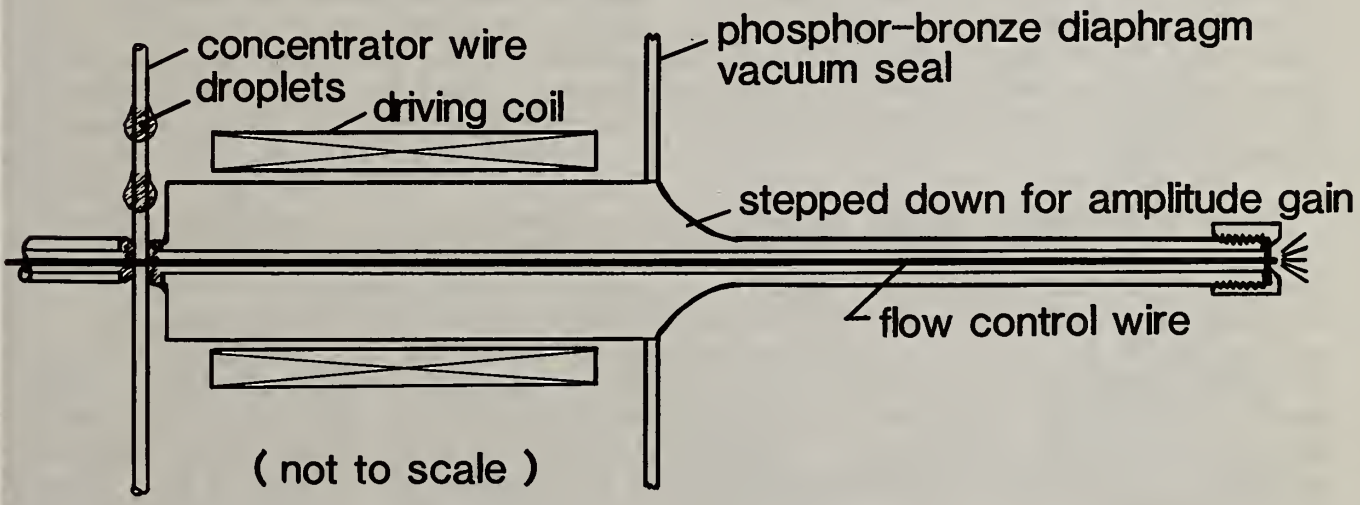


Figure 36. Magnetostrictive sonic atomizing probe for LC/MS.

The first reversed-phase application was that of measuring the polar molecule, valproic acid, in a complex matrix (serum), by direct injection of serum onto the chromatographic column. Other analyses for this compound require extraction from the serum and preparation of a derivative. Preliminary trials of the direct LC/MS method showed precision of about 10 percent relative standard deviation, e.g., 100 ppm ± 10 ppm. If refinements can improve the precision, the method will be used for certifying trace level constituents in forthcoming Standard Reference Materials. Other applications of the LC/MS technique to reversed-phase liquid chromatography are now being pursued.

R. G. Christensen, H. S. Hertz, E. White V

20. Laser Induced Photodissociation of Ions

As part of a five-year mass spectrometry competence building program in "Analysis of Ionization Mechanisms and Ion Structures," we have begun to explore the laser induced photodissociation of ions, particularly the potential for organic structure determination and for analytical specificity.

The photodissociation of ions has been used for some years in conjunction with time-of-flight and ion cyclotron resonance spectrometers, as well as more recently with mass filter spectrometers to investigate absorption cross sections, dissociation pathways, and kinetic energy release. These studies, for the most part, can be classified as physical chemistry and have been limited to low molecular weight compounds. A group under J. H. Beynon [1] has reported in the last year, the laser induced photodissociation of ions using an argon ion laser and conventional double focusing magnetic mass spectrometers of both normal and reversed geometry. The molecules examined have been simple mono- and di-substituted benzenes and interest has centered on kinetic energy release and dissociation as probes of the mechanisms of ion dissociations.

The experimental set-up which we are presently using is shown schematically in figure 37. The mass spectrometer is an existing high resolution instrument of Mattauch-Herzog geometry equipped to allow detection of ions decomposing in the first field-free region (metastable ions) by accelerating voltage scans and by two linked scan methods in which the electrostatic analyzer and magnet are scanned simultaneously. The laser, optical components, and lock-in amplifier, borrowed to test feasibility, are being replaced with more suitable components. An argon ion laser with an output of at least one watt at each of ten wavelengths between 350 and 529 nm (3.47-2.34 eV), is being installed.

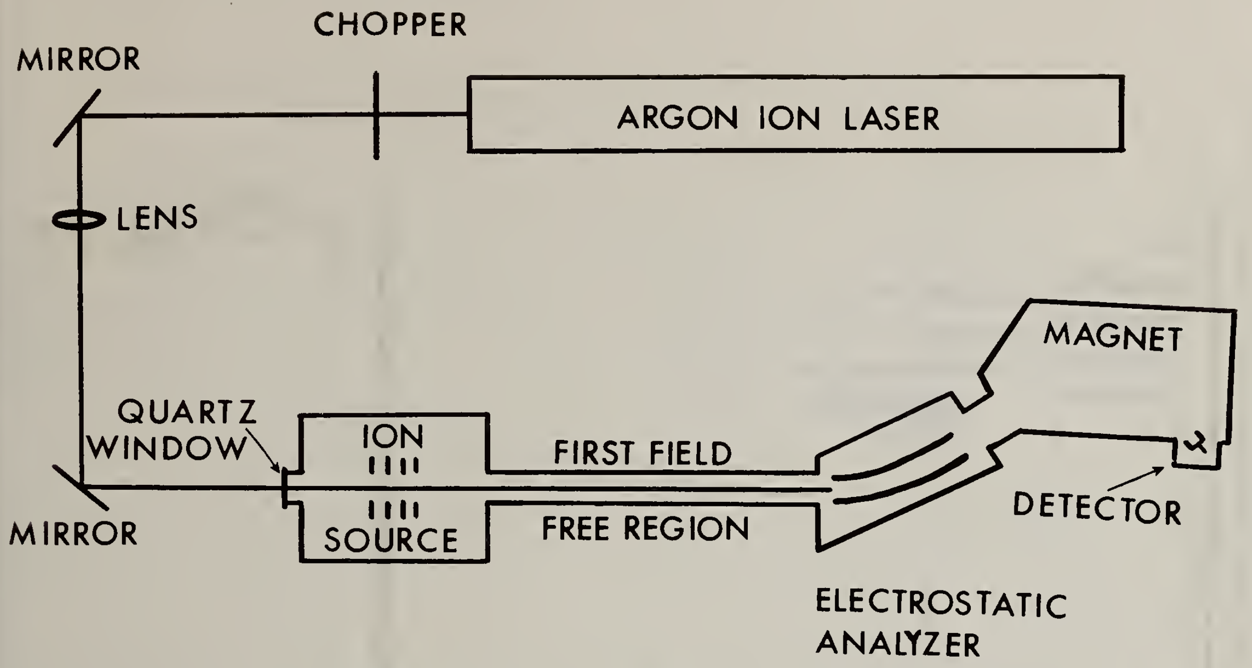


Figure 37. Schematic of the experimental arrangement used for the laser induced photodissociation of ions.

The photodissociation behavior of ions from about a dozen compounds has been examined at 514.5 nm (2.41 eV) using either accelerating voltage or linked electrostatic/magnetic field scans. The pronounced and selective effect of irradiation on the intensities of metastable ions, which leads to the formation of m/z 77 in nitrobenzene, is shown in the accelerating voltage scans in figure 38. Fragmentation pathways not observed in spontaneous metastable ion decompositions also occur. Thus, as may be seen in figure 39, irradiation causes 2,4-hexadiyne molecular ion to lose a methyl radical, a fragmentation also observed by collisional activation. Among other compounds showing laser induced photodissociation were benzene, naphthalene, anthracene, cinnamic acid, N-trifluoroacetylphenylalanine cyclohexyl ester (which was examined as a model for planned studies of peptides), and silver acetate. Compounds not showing any activity at the 514.5 nm wavelength included aliphatic esters, an aliphatic amide, and, unexpectedly, an aromatic compound, phenol.

Planned activities for the near future include installation of the more powerful laser and new optics, automation of data collection which is currently entirely manual, some survey work to find out what kinds of compounds (ions) will show activity and at which wavelengths, and major modification of the mass spectrometer flight tube to permit small-angle crossed-beam experiments. This latter modification will allow photodissociation of ions created by field desorption. The combined techniques should be a powerful method for the determination of the structure of organic molecules.

Reference

[1] Harris, F. M., Mukhtar, E. S., Griffiths, I. W., and Beynon, J. H., Proc. R. Soc. Lond. A374, 461-473 (1981).

H. S. Hertz, D. J. Pereles, J. C. Travis (550), E. White V

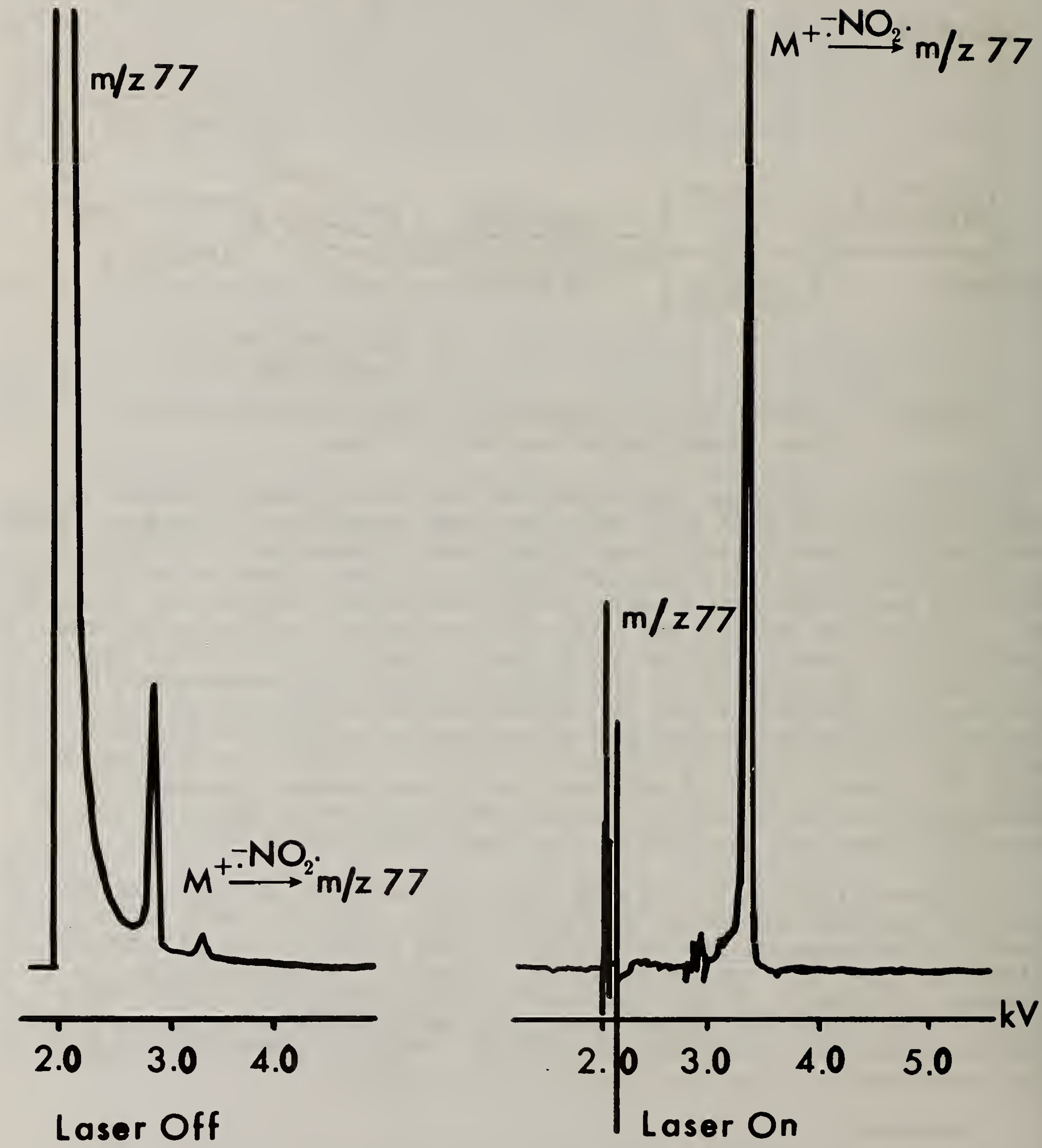


Figure 38. Accelerating voltage metastable ion scans showing the effect of irradiation at 514.5 nm on the loss of NO_2 from nitrobenzene molecular ion.

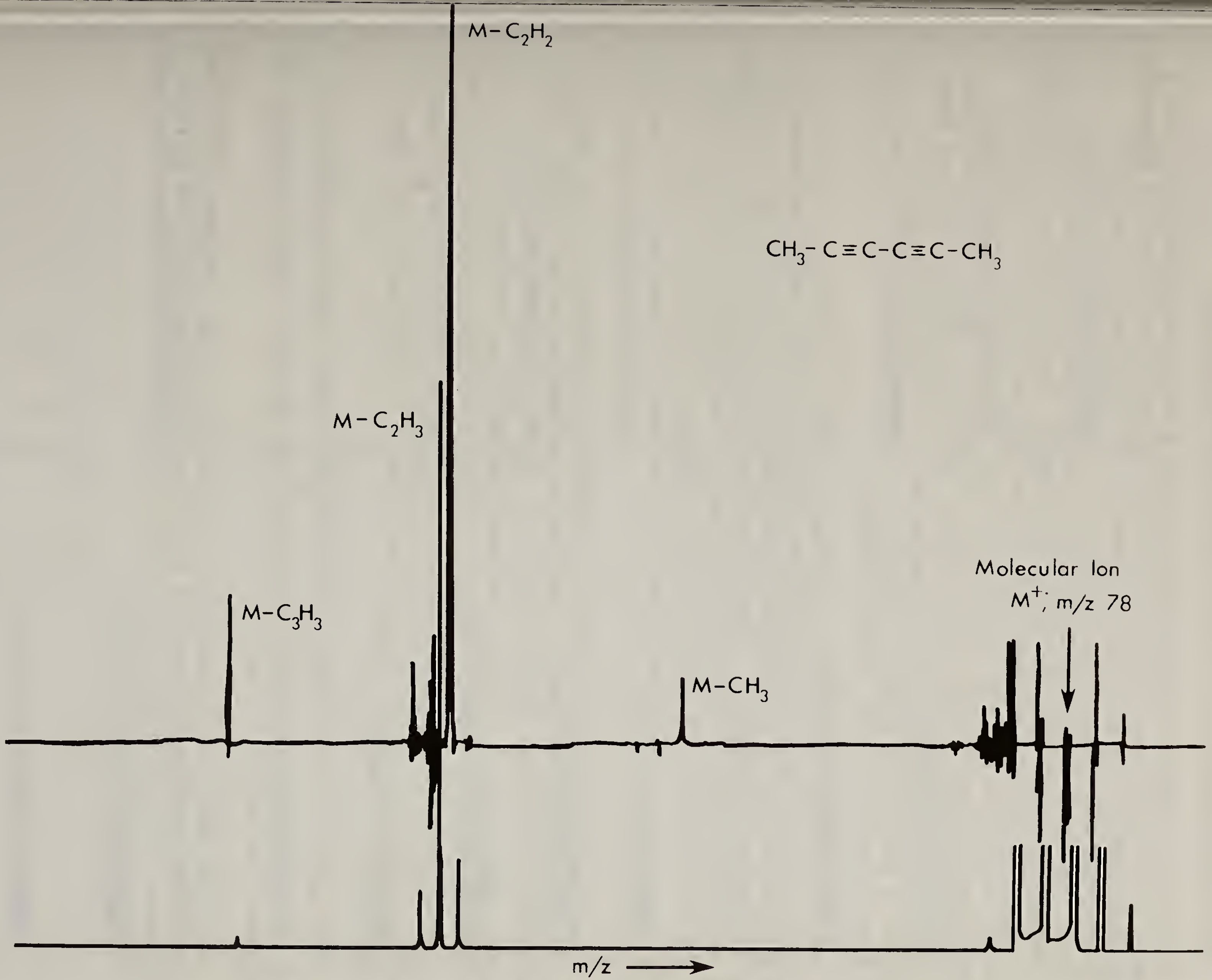


Figure 39. Linked electrostatic analyzer/magnetic field metastable ion scans showing the loss of of methyl from 2,4-hexadiyne. Upper trace: laser on. Lower trace: laser off.

21. A Method for the Mass Calibration of Photoplates in Field Desorption Mass Spectrometry and Its Application to Some Peptides

Exact mass determination by high resolution mass spectrometry has been a valuable tool for structure elucidation and has been widely used for compounds which give electron impact spectra. However, for high mass, nonvolatile molecules, ionization by field desorption is often necessary to obtain a spectrum, and for this method exact mass determination has proved difficult. The common mass calibration material for electron impact, high resolution mass spectrometry, perfluorokerosene (PKF), cannot be used for field desorption since it deactivates the emitters on which the desorption is accomplished. Other procedures such as mass calibration in electron impact, then switching to field desorption, and the use of complex mixtures as calibrants have been used, but are unreliable or very inconvenient. A straightforward way to establish a mass calibration is essential if high resolution, field desorption mass spectrometry is to be routinely useful.

We have developed a method, applicable to field desorption, for establishing a high resolution mass scale on a photoplate by a double exposure in which sample and calibrating material are separately field desorbed onto the same line of the photoplate. Mass calibration is achieved by field desorption of a mixture of silver methanesulfonate and trifluoromethanesulfonate which gives cluster ions of the general formula $[Ag_{m+n+1}(O_3SCH_3)_m(O_3SCF_3)_n]^+$ [1]. These ions provide calibration masses at about every 50 mass units to above 1400 as shown in figure 40.

The precision of the calibration method was evaluated using two pentapeptides, methionine enkephalin, and leucine enkephalin, known to give good low resolution spectra. For 11 spectra of methionine enkephalin with an expected $[M+H]^+$ ion at 574.2335, the measured $[M+H]^+$ was 574.2310 with a standard deviation of 0.0063 (range: 574.2437 - 574.2233); and for 8 spectra of leucine enkephalin with an expected $[M+H]^+$ ion at 556.2771, the measured $[M+H]^+$ was 556.2773 with a standard deviation of 0.0051 (range: 556.2835 - 556.2679).

The accuracy of the method was evaluated by using five polypeptides of known mass. The masses obtained for $[M+H]^+$ and for other ions are compared to the theoretical masses in Table 28.

From the above, we conclude that a mixture of silver methanesulfonate and silver trifluoromethanesulfonate is a good calibrating material and provides satisfactory precision and accuracy for high resolution, field desorption mass spectra using photoplate detection.

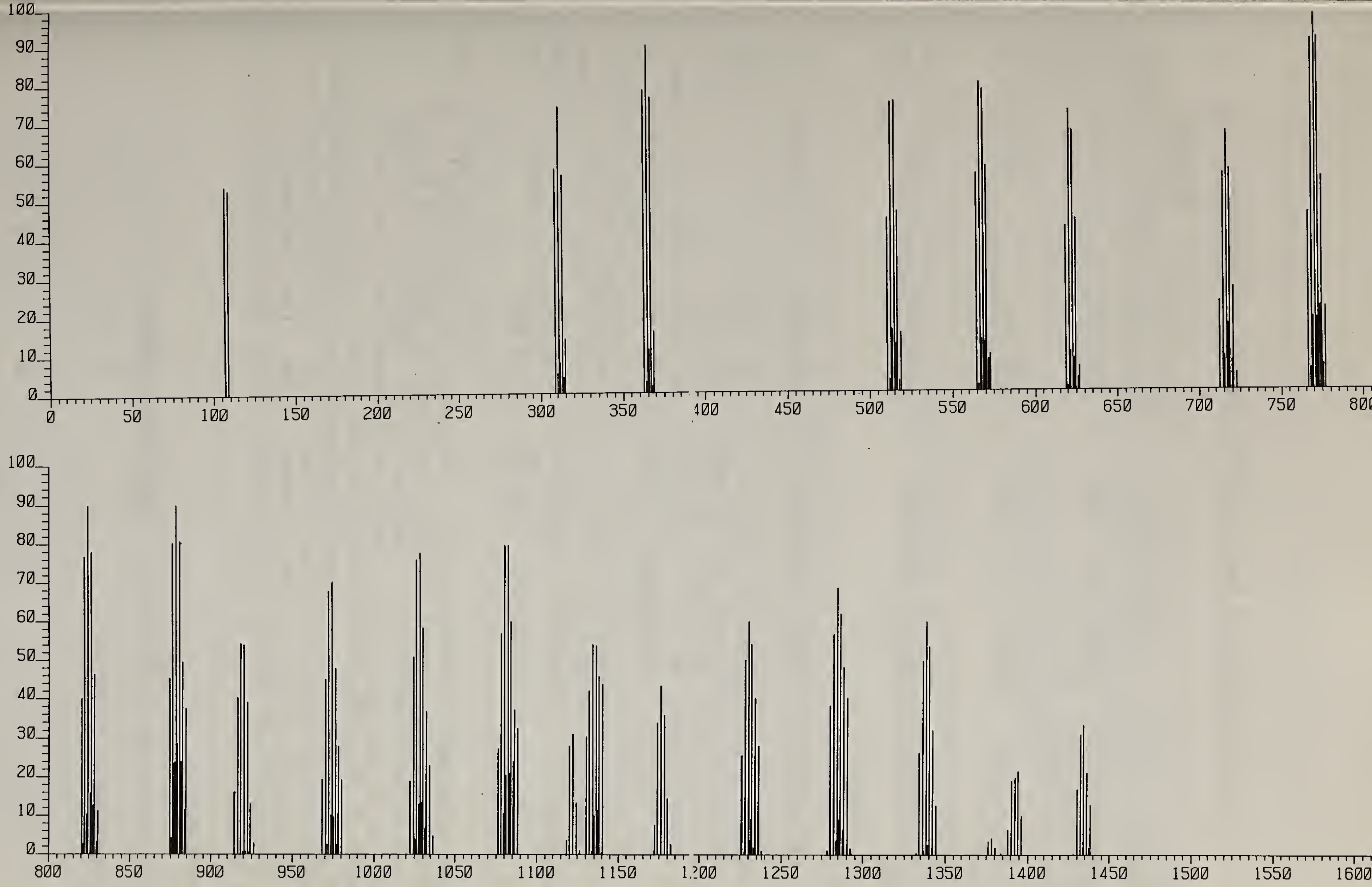


Figure 40. Field desorption mass spectrum of a 1:1 mixture of silver methanesulfonate and silver trifluoromethanesulfonate. Average of 40 exposures on which overexposed lines have been omitted from averaging, thus enhancing the higher mass end of the spectrum.

Table 28. Results of Exact Mass Measurements on Peptides.

Peptide	Theoretical Mass (Mass Units)	Measured Mass (Mass Units)	Measured-Theoretical (Millimass Units)
Trp-Met-Asp-Phe-Amide Gastrin Related Tetrapeptide	$[M+H]^+$: 597.2495	597.2501	0.6
Tyr-Ile-His-Pro-Phe Angiotensin II Pentapeptide	$[M+H]^+$: 676.3459	676.3471	1.2
Lys-Phe-Ile-Gly-Leu-Met-Amide Eledoisin Related Peptide	$[M+H]^+$: 707.4278	707.4187	-9.1
Tyr-Gly-Gly-Phe-Met	$[M+H]^+$: 574.2335	574.2311	-2.4
Met-Enkephalin	$[M+Na]^+$: 596.2155	596.2247	9.2
	$[M+{}^{107}Ag]^+$: 680.1308	680.1287	-2.1
	$[M+{}^{109}Ag]^+$: 682.1304	682.1301	-0.3
	Gly-Phe-Met: 354.1487	354.1483	-0.4
Tyr-Gly-Gly-Phe-Leu	$[M+H]^+$: 556.2771	556.2778	0.7
Leu-Enkephalin	$[M+Na]^+$: 578.2591	578.2559	-3.2
	Gly-Phe-Leu: 336.1922	336.2070	4.8

Some advantages of the method are: calibration is accomplished in the FD mode with no switching between EI and FD required; the calibration material leaves the activated emitter wire undamaged so that sample and calibration material can be desorbed one at a time in either order from an emitter; the components of the calibration material are commercially available; the calibration masses are spaced at reasonable intervals over a large mass range; the mass defect of the calibration material makes sample ions easily distinguishable from calibration ions; and the existence of two silver isotopes at a ratio close to 1 leads to clusters from which lines of appropriate intensity can be chosen.

Reference

[1] Robert, G. D.; White V, E. Unpublished results.

R. Espinosa-Leniz, E. White V

22. Design of a Toxic Chemicals and Carcinogens Handling Laboratory

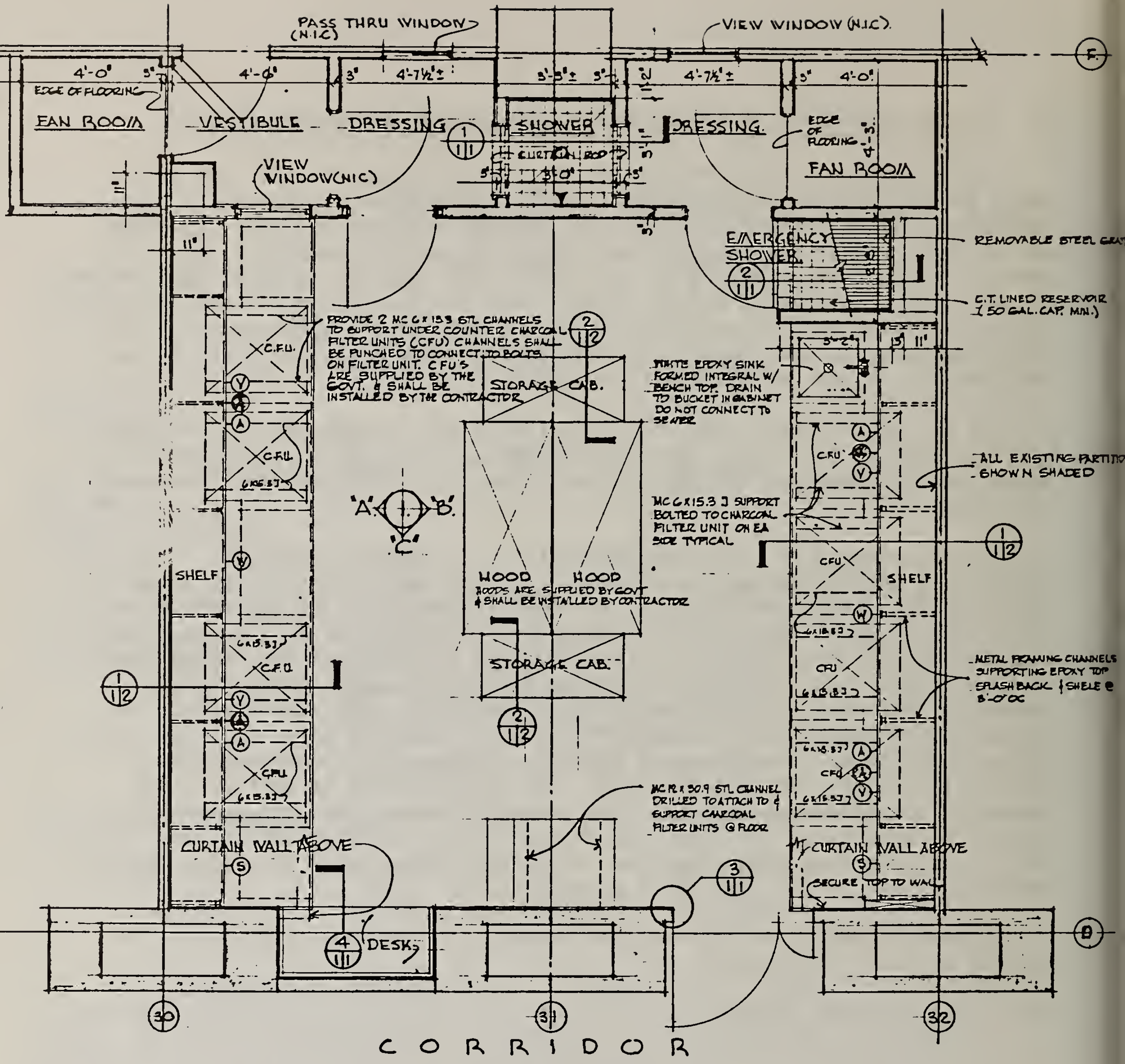
This year the Organic Analytical Research Division finished the design phase for the construction of a toxic and/or carcinogenic chemicals handling laboratory. This facility will be used for the storage, weighing, solution, and chromatographic analyses of these chemicals and will markedly reduce the potential danger for exposure to our staff. The facility is being implemented because (1) an increasing number of toxic and carcinogenic compounds are used in our laboratories, (2) existing laboratory storage and weighing areas for such chemicals are very congested, and (3) a greater number of staff members are required to work with these compounds.

In FY 1981, the services of an architectural and engineering firm (A&E) were procured to design the facility to meet our use plan. During the design phase, numerous meetings of the A&E, NBS scientists, and NBS Plant personnel were held.

The floor plan for the proposed facility is shown in figure 41. The facility is entered through an anteroom in which the user can dress in protective clothing before passing into the inner laboratory. The air flow in the inner laboratory is designed to minimize any contamination of the users from chemicals in the facility. Two Class II, Type II hoods are positioned back to back in the center of the lab and are flanked by custom-built storage cabinets. All air in the laboratory is subjected to both HEPA (particulate removal) and charcoal (vapor removal) filters. The work areas on either side of the facility will hold gas and liquid chromatographic instrumentation (specially vented) for analysis work. The facility will be exited either through a second change room and then through a shower (for shower-out protocols) or through the first change room, thus bypassing the shower. The facility is provided with operation monitoring alarms and a provision for emergency power in the event of a power failure.

During FY 1982, the contract for construction will be sent out for bid and the facility constructed.

S. N. Chesler, H. S. Hertz

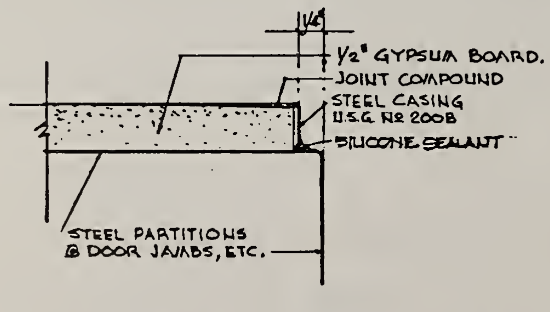


NEW FLOOR PLAN SCALE 1/2"=1'-0"

NOTE: SEAL THE FOLLOWING W/SILICONE SEALANT TO PREVENT AIR MIGRATION INTO OR OUT OF LAB MODULE:
1) PERIMETER OF EXISTING METAL PARTITIONS @ FLOOR, CEILING & ABUTTING WALLS
2) ALL JOINTS IN EXISTING METAL PARTITIONS.
3) ALL PIPE CONDUIT & DUCT PENETRATIONS THRU LAB FLOORS, WALLS & CONC CEILING.
4) INSIDE OF ALL ELECTRICAL CONDUITS PENETRATING THE LAB EXTERIOR ENVELOPE
5) ALL PERIMETER JOINTS OF NEW DRYWALL WALL COVERING (@ CONC FLOOR & CEILING AROUND DOOR JAMBS & ALL OTHER AREAS AS NECESSARY TO PREVENT AIR MIGRATION

BENCH TOP SERVICE LEGEND

Ⓐ	100 lb. AIR
Ⓐ	15 lb. AIR.
Ⓦ	55° WATER
Ⓢ	WASTE
Ⓥ	VACUUM



TYPICAL CASING 3 / 11

Figure 41. Floor plan for the proposed NBS toxic chemicals handling laboratory.

C. Outputs and Interactions (Organic Analytical Research Division)

1. Publications

Brown, J. M., Wise, S. A., and May, W. E., Determination of Benzo(a)pyrene in Recycled Oils by a Sequential HPLC Method, *J. Environ. Sci. Health A15* (6), 613-623 (1980).

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Hertz, H. S., Standard Reference Materials for Trace Organic Environmental Analysis, Abstracts from the 1980 Pittsburgh Conference, Atlantic City, NJ, Paper No. 567 (1980).

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Margolis, S. A. and Longenbach, P. J., Analysis of Purity of Commercial Peptides by High-Resolution Liquid Chromatography, *The Role of Peptides in Neuronal Function*, J. Barker and T. Smith, eds., Marcel Dekker, New York, NY (1980).

Reeder, D. J., Place of Reference Materials and Reference Methods in the Evaluation of Drug Effects, *Drug Effects on Lab. Test Results*, 49-57 (1980).

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Bartle, K. D., Lee, M. L., and Wise, S. A., Modern Analytical Methods for Environmental Polycyclic Aromatic Compounds, *Chem. Soc. Rev. 10* (1), 113-158 (1981).

Brown-Thomas, J. M. and May, W. E., The Analysis of Phenols in Water by High-Performance Liquid Chromatography, Abstracts of the 1981 Pittsburgh Conference, held March 9-13, 1981, Atlantic City, NJ (1981).

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Chesler, S. N., White, P. A., May, W. E., and Parris, R. M., Analysis of Polychlorinated Biphenyls in Waste and Lubricating Oils, Abstracts of the 1981 Pittsburgh Conference, held March 9-13, 1981, Atlantic City, NJ, Paper No. 227 (1981).

Christensen, R. G., Hertz, H. S., Meiselman, S., and White V, E., A Liquid Chromatograph/Mass Spectrometer Interface Incorporating Continuous Sample Preconcentration, *Anal. Chem. 53* (2), 171-174 (1981).

Durst, R. A. and Bates, R. G., Hydrogen Ion Activity, *Encyc. of Chem. Tech.*, 3rd ed., *13*, 1-12 (1981).

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Guenther, F. R., Chesler, S. N., and Parris, R. M., The Quantitative Analysis of Some N-Heterocyclics in Shale Oil by Two-Dimensional $(GC)^2$, Abstracts of the 1981 Pittsburgh Conference, held March 9-13, 1981, Atlantic City, NJ, Paper No. 45 (1981).

Guenther, F. R., Parris, R. M., Chesler, S. N., and Hilpert, L. R., The Determination of Phenolic Compounds in Alternate Fuel Matrices, *J. Chromatog. 207*, 256-261 (1981).

Hancock, D. K., Literature Survey Characterization of Petroleum Derived Oils by Luminescence Spectroscopy, Internal Report for the NBS Recycled Oil Program (1981).

Harrison, S. H., Zeisler, R., and Wise, S. A., Project Summary: Pilot Program for the National Environmental Specimen Bank - Phase I, *EPA Res. Report* (1981).

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Schaffer, R., Mandel, J., Sun, T., Cohen, A., and Hertz, H. S., Evaluation of the AACC Candidate Reference Method for Serum Glucose vs an ID/MS Method, to be published as an NBS Special Publication.

Blubaugh, E. A., and Doane, L. M., A Vacuum Thin Layer Electrochemical Cell for Nonaqueous Spectroelectrochemistry, Anal. Chem., in press.

Christensen, R. G., Hertz, H. S., Reeder, D. J., and White V, E., Developments in the Analysis of Priority Pollutants by Liquid Chromatography/Mass Spectrometry and Immunoassay Procedures, Adv. in the Identification and Anal. of Org. Poll. in Water 1, Lawrence H. Keith, ed., Ann Arbor Science Publishers, Ann Arbor, MI, in press.

Doane, L. M. and Fatiadi, A. J., Electrochemical Oxidation of Several Oxocarbon Salts in N,N-Dimethylformamide, J. Electroanal. Chem. and Interfacial Electrochem., in press.

Doumas, B. T., Bayse, D. D., Carter, R. J., Peters, T., Jr., and Schaffer, R., A Reference Method for the Determination of Total Serum Protein. I. Development and Validation, Clin. Chem. 27, in press.

Doumas, B. T., Bayse, D. D., Bauer, K., Carter, R. J., Elevitch, F., Garber, C. C., Graby, R. A., Hause, L. L., Mathes, A., Peters, T., Jr., Rand, R. N., Reeder, D. J., Russell, S. M., Schaffer, R., and Westgard, J. O., A Reference Method for the Determination of Total Protein. II. Test for Transferability, Clin. Chem. 27, in press.

Durst, R. A., Views on the Current Status of the pH Scale, Blood pH, Carbon Dioxide, Oxygen, and Calcium-Ion, O. Siggaard-Andersen, ed., Copenhagen, in press.

Durst, R. A. and Maienthal, E. J., Sampling Operations for the Pilot Environmental Specimen Bank, IAEA Report, in press.

Durst, R. A., Siggaard-Andersen, O., and Maas, A. H. J., Reference and Quality Control Materials for pH and Blood Gases, Blood pH, Carbon Dioxide, Oxygen, and Calcium-Ion, O. Siggaard-Andersen, ed., Copenhagen, in press.

Harrison, S. H., Zeisler, R., and Wise, S. A., Pilot Program for the National Environmental Speciman Bank - Phase I, EPA Res. Report, in press.

Konash, P. L., Wise, S. A., and May, W. E., Selective Quenchofluorometric Detection of Fluoranthenic Polycyclic Aromatic Hydrocarbons in High-Performance Liquid Chromatography, J. Liq. Chromatog., in press.

MacCrehan, W. A. and Durst, R. A., Dual-Electrode Liquid Chromatographic/Electrochemical Detector for the Determination of Analytes with High Redox Potentials, Anal. Chem., in press.

Schaffer, R., Velapoldi, R. A., Paule, R. C., Mandel, J., Bowers, G. N., Jr., Copeland, B. E., Rodgerson, D. O., and White, J. C., Reference Method for Determination of Serum Sodium, Clin. Chem., in press.

Sonnefeld, W. J., Zoller, W. H., May, W. E., and Wise, S. A., On-Line Multidimensional Liquid Chromatographic Determination of Polycyclic Aromatic Hydrocarbons, Anal. Chem., in press.

Wise, S. A., High-Performance Liquid Chromatography for the Determination of Polycyclic Aromatic Hydrocarbons, Chapter 5 in Handbook for Polycyclic Aromatic Hydrocarbons, A. Bjørseth, ed., Marcel Dekker, New York, NY, in press.

Wise, S. A., Bonnett, W. J., Guenther, F. R., and May, W. E., A Relationship Between Reversed-Phase C_{18} Liquid Chromatographic Retention and the Shape of Polycyclic Aromatic Hydrocarbons, J. Chromatog. Sci., in press.

Yap, W. T. and Durst, R. A., Electron Transfer in Molecules with Interacting Multiple Redox Centers, J. Electroanal. Chem., in press.

Schaffer, R., Sniegoski, L. T., Welch, M. J., White V, E., Cohen, A., Hertz, H. S., Mandel, J., Paule, R. C., Svensson, L., Bjørkhem, I., and Blomstrand, R., Comparison of Two Isotope Dilution/Mass Spectrometry Methods for the Comparison of Total Cholesterol, Clin. Chem., submitted for publication.

2. Talks

S. A. Margolis, "Nutrient Analysis Standards," Interagency Technical Committee (IATC) Working Group on Nutrient Composition of Foods, National Institutes of Health (NIH), Bethesda, MD, Sept. 10, 1980.

W. E. May, "Quality Assurance in Environmental Trace Organic Analysis," Chemistry Department, University of Maryland, College Park, MD, Sept. 12, 1980. Invited

E. White V, "High Resolution and Field Desorption Mass Spectrometry," Department of Chemistry, University of Maryland, College Park, MD, Sept. 12, 1980.

S. A. Wise, "The Environmental Specimen Bank Program," EPA/Narragansett Seminar, Narragansett, RI, Sept. 15, 1980. Invited

S. A. Wise, "The Relationship of Liquid and Gas Chromatographic Retention and the Shape of Polycyclic Aromatic Hydrocarbons," Washington Chromatography Discussion Group, Hewlett-Packard Company, Rockville, MD, Sept. 18, 1980. Invited

M. L. Fultz, "A Study of the Spectroelectrochemistry of o-Tolidine Using a Vidicon Detector," 1980 Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, PA, Oct. 1, 1980.

W. A. MacCrehan, "A Dual Electrode Reductive Electrochemical Detector for Liquid Chromatography," 1980 Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, PA, Oct. 1, 1980.

P. A. White, "The Certification of Generator Columns for the Production of Aqueous Polynuclear Aromatic Hydrocarbon Standards - SRM 1644," 1980 Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, PA, Oct. 2, 1980.

H. S. Hertz, "Determination of Individual Organic Compounds in Shale Oil," University of Maryland, College Park, MD, Oct. 3, 1980. Invited

E. A. Blubaugh, "Asymmetric Schiff Base Complexes of Nickel (II) and Copper (II)," Electrochemical Society Meeting, Washington, DC, Oct. 4, 1980.

S. A. Wise, "A Relationship Between Reversed-Phase C_{18} Liquid Chromatographic Retention and the Shape of Polycyclic Aromatic Hydrocarbons," International Symposium on Advances in Chromatography, Houston, TX, Oct. 7, 1980.

H. S. Hertz, "Quantitative Trace Organic Analysis," Chemistry Department, Northeastern University, Boston, MA, Oct. 27, 1980. Invited

W. A. MacCrehan, "Detection of Reducible Analytes Separated by Liquid Chromatography Without Rigorous Oxygen Exclusion," Eastern Analytical Symposium, New York, NY, Nov. 21, 1980.

L. T. Sniegoski, "The Use of Isotope Dilution/Mass Spectrometry for the Accurate Determination of Organic Constituents in Serum," 15th American Chemical Society Middle Atlantic Regional Meeting, Washington, DC, Jan., 1981, with A. Cohen, H. S. Hertz, R. Schaffer, M. J. Welch, and E. White V.

W. E. May, "High-Performance Liquid Chromatographic Methods for Trace Organic Analysis," Chemistry Department, Howard University, Washington, DC, Jan. 23, 1981. Invited

H. S. Hertz, "Quantitative Analysis of Individual Trace Organic Compounds in Shale Oil," Hewlett-Packard GC/MS User's Meeting, Baltimore, MD, March 6, 1981. Invited

F. R. Guenther, "The Quantitative Analysis of Some N-Heterocyclics in Shale Oil by Two-Dimensional $(GC)^2$," 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 9, 1981.

D. J. Reeder, "Fluoroimmunoassay for Detection of Dinitrophenols in Water," 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 9, 1981.

J. M. Brown-Thomas, "The Analysis of Phenols in Water by High-Performance Liquid Chromatography," 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 10, 1981.

R. M. Parris, "Analysis of Polychlorinated Biphenyls in Waste and Lubricating Oils," 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 10, 1981.

W. E. May, "Analysis of Polycyclic Aromatic Hydrocarbons in Water: Standards Methods or Standard Reference Materials," 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 12, 1981. Invited

D. J. Reeder, "An Overview of Analytical Chemistry and Immunoassay at the National Bureau of Standards," Chemistry Department, North Texas State University, Denton, TX, March 16, 1981. Invited

W. E. May, "Analysis of Selected Organics in Alternate Fuels Using Multidimensional HPLC Techniques," Perkin-Elmer Corporation, Norwalk, CT, April 21, 1981. Invited

S. A. Wise, "Analytical Methods for Polycyclic Aromatic Hydrocarbons in Air Particulates," EPA National Symposium on Monitoring Hazardous Organic Pollutants in Air, Raleigh, NC, April 30, 1981. Invited

S. A. Wise, "The Determination of Polycyclic Aromatic Hydrocarbons by High-Performance Liquid Chromatography," Department of Chemistry, University of Oslo, Oslo, Norway, May 14, 1981. Invited

S. A. Wise, "Trace Organic Analysis at the National Bureau of Standards," Department of Chemistry, University of Oslo, Oslo, Norway, May 14, 1981. Invited

S. A. Wise, "The Determination of Polycyclic Aromatic Hydrocarbons by High-Performance Liquid Chromatography," Central Institute for Industrial Research, Oslo, Norway, May 15, 1981. Invited

S. A. Wise, "Certification Analysis of Environmental Standard Reference Materials," Colloquium for Chemie and Okologische Chemie, Technische Universität Weinhenstephan, Weinhenstephan, Germany, May 18, 1981. Invited

S. A. Wise, "Organic Analysis in the NBS Pilot Environmental Specimen Bank Program," Annual Environmental Specimen Banking Meeting sponsored by U.S. EPA and Umweltbundesamt of Federal Republic of Germany, Kernforschungsanlage (Nuclear Research Center)KFA, Jülich, Germany, May 20, 1981. Invited

S. A. Wise, "Mussel Sampling, Storage, and Analysis for the Pilot Environmental Specimen Bank - Current Status," Annual Environmental Specimen Banking Meeting sponsored by U.S. EPA and Umweltbundesamt of Federal Republic of Germany, Kernforschungsanlage (Nuclear Research Center)KFA, Jülich, Germany, May 20, 1981. Invited

M. J. Welch, "The Certification of Organic Analytes in a Human Serum Standard Reference Material by ID/MS," American Society for Mass Spectrometry 29th Annual Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, May 26, 1981.

L. R. Hilpert, "Analysis of Phenolic and Polynuclear Aromatic Hydrocarbon Species in Alternate Fuels and Effluents," American Society for Mass Spectrometry 29th Annual Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, May 28, 1981.

R. Espinosa-Leniz, "A Method for the Mass Calibration of Photoplates in Field Desorption and Its Application to Some Peptides," American Society for Mass Spectrometry 29th Annual Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, May 28, 1981.

E. A. Blubaugh, "Technetium Electrochemistry: Electrochemical Studies of Arphos Complexes of Technetium in Nonaqueous Media," Naval Research Laboratories, Washington, DC, July 6, 1981. Invited

E. A. Blubaugh, "Technetium Electrochemistry: Electrochemical Studies of Arphos Complexes of Technetium in Nonaqueous Media," E. R. Squibb and Sons, Inc., The Squibb Institute for Medical Research, New Brunswick, NJ, Aug. 6, 1981. Invited

R. E. Botto, "High-Field Proton and Nitrogen-15 NMR Spectroscopy of Neomycin B, New York, NY, Aug., 1981, with B. Coxon.

B. Coxon, "Two-Dimensional Proton NMR Spectroscopy of Hydroxyl Proton Coupled α- and β-Glucopyranoses at 400 MHz, New York, NY, Aug., 1981.

B. Coxon, "Structural Analysis of Fortimicin Antibiotics by Means of Proton Coupled Nitrogen-15 NMR Spectra, New York, NY, Aug., 1981, with J. B. McAlpine.

R. M. Davidson, "Nitrogen-15 NMR and Mass Spectral Characterization of Some Doubly ^{15}N-Labeled ($^{15}N_2$-) 2-Amino Oxazoline Derivatives of the Pentoses and Hexoses," American Chemical Society Meeting, New York, NY, Aug. 26, 1981.

R. A. Durst, "Assessment of the Status of Spectroelectrochemistry," 31st General Assembly of the International Union of Pure and Applied Chemistry (IUPAC), Catholic University, Leuven, Belgium, Aug. 27, 1981. Invited

R. A. Durst, "The International Practical pH Scale," 31st General Assembly of the International Union of Pure and Applied Chemistry (IUPAC), Catholic University, Leuven, Belgium, Aug. 28, 1981. Invited

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

Bruce Coxon
- Secretary, ASTM, Subcommittee 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, ASTM, Committee D19 on Water
- 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

Barbara F. Howell
- Alternate Councilor, ACS
- Treasurer, ACS of Washington, DC
- Member, ASTM, Committee E7 on Nondestructive Testing
  - Subcommittee E7.03 on Liquid Penetrant and Magnetic Particle
    - Task Group E07.03.02 on Magnetic Particle and Penetrant Testing--Penetrant Method
    - Task Group E07.03.05 on Magnetic Particle and Penetrant Testing
    - Task Group E07.03.06 on Magnetic Particle Methods
    - Task Group E07.03.07 on Magnetic Particle and Penetrant Testing--Magnetic Glossary

Willie E. May
- Member, ASTM, Committee D19 on Water
- President, Washington Chromatography Discussion Group

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 9, 1980	-	Bruce Coxon and Robert E. Botto, National Bureau of Standards, "NMR Experiments on the 400 MHz Instrument".
October 23, 1980	-	Alexander J. Fatiadi, National Bureau of Standards, "Croconate Semiconductors".
October 28, 1980	-	Ronald L. Birke, City College of New York, "Surface Enhanced Raman Spectroscopy".
December 17, 1980	-	Ronald L. Birke, City College of New York, "Diagnosis of Electrode Kinetic Parameters by Differential Pulse Polarography".
February 12, 1981	-	Mark Wrighton, Massachusetts Institute of Technology, "Chemically Modified n-Type Semiconducting Silicon Photoelectrodes".
February 19, 1981	-	Robert McKinney, National Institutes of Health, "Containment and Safe Handling of Carcinogens and Biological Hazards".
February 24, 1981	-	George M. Frame, U.S. Coast Guard Research Development Center, "A Mobile Laboratory for Fast Response to Spills".

March 5, 1981 - Dennis J. Reeder, National Bureau of Standards, "Immunoassay Procedures: FIA, EIA, ELISA, Etc".

March 13, 1981 - Milton L. Lee, Brigham Young University, "Recent Advances in Capillary Chromatography".

April 15, 1981 - William J. Sonnefeld and Franklin R. Guenther, National Bureau of Standards, "Multidimensional Chromatography".

May 14, 1981 - Stephen N. Chesler, National Bureau of Standards, "Capabilities of the FTIR".

May 21, 1981 - Norbert Blanckaert, Katholieke Universiteit, Belgium, "The Glucuronic Acid Conjugates of Bilirubin".

June 5, 1981 - C. J. Porter, University College of Swansea, Great Britain, "Consecutive and Charge Stripping Reactions in Mass Spectrometry".

August 5, 1981 - Josef K. F. Huber, University of Vienna, Austria, "Quantitative Analysis Using Multidimensional Chromatography".

August 5, 1981 - P. Ramachandra Naidu, Sri Venkatesware University, India, "Chlorosulphonic Acid as a Titrant in Non-aqueous Media".

August 20, 1981 - Robert M. Davidson, National Bureau of Standards, "Nitrogen-15 NMR and Mass Spectral Characterization of Some Doubly ^{15}N-Labeled ($^{15}N_2$-) 2-Amino Oxazoline Derivatives of the Pentoses and Hexoses".

September 17, 1981 - Marianne Grassl, Boehringer Mannheim Biochemicals, Germany, "Quality Control of Biochemicals".

b. Conferences Sponsored

October 23-24, 1980 - S. A. Margolis, Workshop on Reference Materials for Organic Nutrient Measurement, National Bureau of Standards, Washington, DC.

c. Seminars Organized

H. S. Hertz, The Search for Zero, FDA Mass Spectrometry Symposium, Food and Drug Administration, Washington, DC, October 15-17, 1980.

H. S. Hertz, Analytical Chemistry Sessions, 15th American Chemical Society Middle Atlantic Regional Meeting, Washington, DC, January 7-9, 1981.

H. S. Hertz, EPA National Symposium on Monitoring Hazardous Organic Pollutants in Air, Session IV -- Sampling and Analytical Techniques for Organic Aerosols, Raleigh, NC, April 28 - May 1, 1981.

H. S. Hertz, and E. White V, Interpretation of Mass Spectra and Quantitative Mass Spectrometry, sponsored by the American Society for Mass Spectrometry, Minneapolis, MN, May 23-24, 1981.

d. SRM Certification

1) SRM 909, Human Serum
2) SRM 910, Sodium Pyruvate
3) SRM 938, 4-Nitrophenol
4) SRM 998, Angiotensin I (In Process)
5) SRM 1564, Indeno(1,2,3-cd)pyrene Generator Columns (In Process)
6) SRM 1581, Polychlorinated Biphenyls in Oil (In Process)
7) SRM 1590, Stabilized Wine
8) SRM 1595, Tripalmitin (In Process)
9) SRM 1599, Valproic Acid and Carbamazepine in Human Serum (In Process)
10) SRM 1644, Generator Columns for PAH in Water
11) SRM 1647, Polynuclear Aromatic Hydrocarbons in Acetonitrile
12) SRM 1649, Polynuclear Aromatic Hydrocarbons in Air Particulate Matter (In Process)
13) SRM 1815a, n-Heptane (Engine Octane Number Standard)

IV. Gas and Particulate Science Division

Harry L. Rook, Chief
Raymond L. McKenzie, Deputy Chief

A. Division Overview

The Gas and Particulate Science Division develops 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 five groups with scientific effort divided approximately equally between gas analytical research and microanalytical research. The group structure and personnel alignment are given in the Division organization chart.

During the past year, a number of major achievements have been realized. The Microanalysis Research Group has made excellent progress in quantitative compositional mapping. Using the electron microprobe, accurate two-dimensional mapping has been demonstrated and applied to grain boundry migration studies. Changes in zinc-copper concentrations at boundry sites are clearly evident with micrometer resolution. Also a substantial improvement has been made in the elemental ratio technique using the ion microprobe. Accurate depth distributions of arsenic in silicon have been demonstrated.

Other significant outputs include: the development of the first set of test thin film standards for analytical electron microscopy and laser microprobe mass analyzer (LAMMA) studies; the determination of scaling factors leading to quantitative laser Raman microanalysis on selected samples; the development of accurate expressions for atomic number and energy dependence of x-ray bremsstrahlung; investigations into the effects of crystal orientation in quantitative secondary ion microscopy; and investigations into ion yield mechanisms in the laser excitation process of LAMMA.

In x-ray fluorescence the group has completed the development of a comprehensive set of interelement corrections to improve the accuracy of energy-dispersive x-ray spectrometric analysis. These, coupled with an improved line overlap correction procedure, have significantly improved the accuracy of self-consistent compositional calculations of XRF data.

In the area of gas measurement and analytical research, a major achievement during the past year was the completion of the infrared diode laser photometer. A procedure has been developed for the direct analysis of trace levels of N_2O using the new system. The diode laser results have been compared to results obtained by electron capture gas chromatography with good agreement. This successful utilization of two independent analytical methods to obtain accurate gas mixture concentrations represents a significant advance from the current practice of basing gas mixture composition on gravimetric formulation data. This measurement achievement will have significant impact on the measurement of reactive gaseous species in contained mixtures and in the atmosphere. A second laser photometric technique using opto-acoustic signal detection has also been used successfully to determine low concentrations of NO_2 in the presence of high concentrations of NO and nitrogen. This work was vital to the analytical certification process of NO_2 gas SRM's. Finally, the first comprehensive determination of the ozone cross sections from 240 to 340 nm at low temperature has been completed. These data are being used to revise model calculations of ozone cross sections at stratospheric temperatures for use with SBUV satellite ozone monitoring of the earth's atmosphere.

As in past years, the Division has been a major contributer to the NBS SRM program both in research leading to new standards and in the analytical certification process of current SRM's. Over 4000 individual samples of more than 100 different SRM's have been analyzed for SRM certification this year.

The future research directions of the Division may be classified into two general areas. The first is research to improve quantitative microanalytical techniques and methods and to apply those improvements to compositional mapping and particle analysis. The second is research to improve techniques for the accurate analysis of gaseous species in contained mixtures or under atmospheric conditions.

The research directions in microanalysis have been strongly influenced by the equipment-intensive nature of the field. During the past few years, the Division has acquired an assemblage of state-of-the-art microanalytical instrumentation not available at any other single research establishment in the world. At the same time, a small but highly motivated group of research analytical chemists with experience in complementary areas of microanalysis are establishing the foundation for exciting research in new analytical areas that include: three dimensional compositional mapping; automated imaging of particles by elemental or isotopic composition; multiparameter analysis of individual particles using two or more microanalytical techniques with data correlation done under computer control; and the accumulation and reduction of very large multielement data sets derived from arrays of particulate material or from predetermined arrays in two or three dimensional space. In order to build on the research in the above areas, efforts will be made to reassign some Division personnel and to selectively add staff in key areas.

The future directions in gas analytical research have been influenced by numerous personnel changes during the past year. Key research scientists in both the Gas Metrology Group and the Atmospheric Chemistry Group have left the Division as a result of the NBS reduction in force or attrition. However, a firm committment to improve gas measurement techniques remains as the basis of research planning. It is important to note that contained gas mixture standards can still be compounded by gravimetry far more accurately than present analytical techniques can measure them. Research on gas analytical techniques which have the potential of definitive accuracy and high precision has been initiated and will be continued. Optical photometric techniques using ultraviolet, visible, and infrared radiation are showing great promise. Research on gas chromatographic detection theory and response characteristics will also be pursued.

A new research program will be started next year in interfacial stability and surface reactions as they affect gas mixture stability. Initial research will be conducted on oxides of nitrogen. Surface studies will include model as well as real materials. A complete material balance will be attempted to account for losses of gas species of interest.

In summary, the potential for excellent research in gas analysis and in microanalysis must be exploited by present research personnel in the near term and a dedicated management effort must be made to identify key positions which must be filled in the longer term.

1. Microanalysis Research Group: Overview

The Microanalysis Research Group conducts research to advance the development and application of microanalysis techniques for the chemical, crystallographic, and morphological characterization of matter on a micrometer scale of spatial resolution. The techniques utilized include electron probe x-ray analysis, scanning electron microscopy, electron diffraction, electron energy loss spectrometry, secondary ion mass spectrometry, micro-Raman spectroscopy, and laser microprobe mass analysis. Research is conducted on several aspects of each technique including: (1) advancing understanding of the basic physics of the primary excitation and secondary radiation attenuation; (2) developing methods of quantitation; (3) developing standards; and (4) applying results of the research to developing improved compositional mapping techniques and to interface with other selected problems.

A major highlight of the past year has been the expansion of the instrumentation and support facilities of the Microanalysis Research Group. This expansion has been achieved through a combination of initiation of activities in the NBS competence building program on Compositional Mapping and other agency support. The Group now has available a wide range of state-of-the-art microprobe instrumentation, employing primary beams of electrons, ions, or photons and detecting as analytical signals the x-rays, ions, or scattered photons produced during interaction with the sample. During FY81, the Group received the first laser microprobe mass analyzer (LAMMA) in North America (described below) and has arranged for the procurement of a Cameca IMS-3F ion microscope, an advanced secondary ion mass spectrometer. To aid in the development of compositional mapping techniques, a powerful DEC VAX super-mini computer has been obtained and will be augmented with an image processing peripheral which is currently being procured. To ensure that the central processing computer is not overburdened by instrument control functions, the major microprobe instruments (ion microprobe, electron probe microanalyzer, laser microprobe mass analyzer, laser Raman microprobe, and analytical electron microscope) have been individually automated through the use of small minicomputers, which together with the central computer will comprise the Microanalysis Data Collection and Processing System (MADCAPS). The eventual goal of this system is to provide the capability for the preparation of analytical compositional maps in two and possibly three dimensions, with the further possibility of merging information from two or more techniques to improve the overall characterization of the sample.

The development of lateral and depth compositional mapping depends, of course, on the development of reliable methods of quantitative analysis at point locations. Consequently, Group activities have included: (1) the development of trial materials to serve as thin film standards for analytical electron microscopy and laser microprobe mass analysis; (2) the investigation of working curves for the quantitative analysis of inorganic compounds by laser Raman microanalysis; (3) the continuing investigation of accurate expressions for the atomic number and beam energy dependence of the x-ray bremsstrahlung; (4) investigation of crystallographic effects on secondary ion yield in the ion microprobe; and (5) investigation of the parameters which control the ion yield in laser microprobe mass analysis.

The development of candidate materials to serve as thin film standards for analytical electron microscopy and laser microprobe mass analysis represents another step in the Group's efforts to produce "high technology standards" in response to the new analytical techniques which have recently evolved. Previous developments in this series include the Research Material Microanalysis Glasses, Fine Glass Fibers, and Spherical Glass Particles. The new thin films mark the first time we have attempted to develop a material which can be characterized both with regard to composition and dimensions; we seek to provide a known quantity of atoms in a defined volume. We expect that these thin film standards may find uses in techniques other than AEM and LAMMA, especially when combined with the bulk glasses, fibers, and microspheres to provide a wide range of geometrical shapes with which to test and develop instrumentation and analytical techniques.

Finally, a component of the Group's research has been devoted to applications of analysis in support of research activities of other Centers at NBS and other federal agencies including: (1) investigation of rapidly solidified alloys (CNIR); (2) analysis of stratospheric aerosols (NASA); (3) analysis of foreign debris in human tissue (FDA); (4) study of dopant redistribution during laser annealing of semiconductors (CEE); (5) preparation of trial standards for asbestos mineral analyses (EPA); and (6) studies of the mechanisms of grain boundary migration (CMR).

Future research plans of the group are strongly influenced by the competence program in compositional mapping and plans for new high technology standards. Plans for the coming year include continued research on three dimensional compositional mapping, multiparameter analysis of arrays of individual particles, research on automated immage analysis, and continued research on their film standards.

Dale E. Newbury, Group Leader; Adville A. Bell, 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 Spectrometry Group: Overview

The X-Ray Fluorescence Spectrometry Group conducts research in sample preparation including preconcentration methodology applied to a wide range of sample types, develops new techniques for instrument calibration and standardization, develops data reduction procedures for quantitative x-ray analysis, and conducts certification analyses on a wide variety of NBS Standard Reference Materials.

In 1981, the X-Ray Fluorescence Spectrometry Group devoted a major effort to completing EXFNBS — a comprehensive interelement correction and x-ray line overlap computer program for energy-dispersive x-ray spectrometric analysis. We have performed alloy analyses using EXFNBS and compared the results obtained with another fundamental parameter program and the Rasberry-Heinrich method. A technical paper describing this intercomparison has been submitted for publication. In addition, an overview of EXFNBS will also be published. 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.

Next year we plan to investigate the use of toroidal monochromators in energy-dispersive spectrometry to improve detection limits for ultratrace analytical applications, and to install our recently purchased data acquisition system for processing x-ray spectral data.

Peter A. Pella, Group Leader; Feng Ling-Yuan, Anthony A. Marlow,
John S. Sieber

3. Atmospheric Chemistry Group: Overview

The Atmospheric Chemistry Group conducts research on measurement techniques for molecular species at ambient concentrations. This research includes the determination of fundamental constants required for spectroscopic measurements, molecular cross sections, line intensities, and improved trace radioactive gas measurements. The results of this research are applied to the development of improved techniques for trace and ultratrace gas measurement.

Major accomplishments this year in the area of spectroscopy include: (1) the determination of the temperature dependence of the ozone absorption cross-section in the Hartley and Huggin Bands (240 to 340 nm) at 298 K and 243 K; (2) the calibration of the Fourier transform infrared spectrometer (FT-IR) and its application to the first reported determinations of the band intensities of HNO_2 and N_2O_3; (3) continued detailed intercomparison of O_3, NO, and NO_2 measurement standards by gas phase titration; and (4) use of optoacoustic spectroscopy to provide a primary calibration of an NO_2-to-NO converter used for SRM calibration measurements in a cooperative study with the Gas Metrology Group.

A major computer modeling study has been completed this year to evaluate 47 potential chemical reactions occuring in ozone generation systems as a result of impurities in "clean air" sources. The relative levels of interfering products and competing reactions with respect to gas phase titration measurements of O_3, NO, and NO_2 have been evaluated.

In the area of nuclear environmental chemistry, significant activities during the past year have included: (1) analysis of environmental samples obtained from Russia, the Shenandoah Valley, and Houston to determine the relative proportions of contemporary and fossil carbon in order to establish the sources of the samples; (2) research to develop microchemical techniques of sample preparation for Accelerator Mass Spectrometry measurements of microgram size samples; and (3) the organization of a Symposium (ACS, Houston, 1980) on Nuclear and Chemical Dating Techniques (by Dr. Lloyd Currie).

The major emphases next year will be (1) the continued application of optoacoustic and related spectroscopic techniques and of the FT-IR with a long-path cell for the measurement of trace-level atmospheric molecular species, (2) the application of Accelerator Mass Spectrometry for the determination of carbon isotopic ratios in microgram-size samples, and (3) the development of mathematical methods for accurate low-level signal extraction from high backgrounds and for modeling of complex chemical composition matrices from environmental-study data bases.

Raymond L. McKenzie, Acting Group Leader; Arnold M. Bass, Ilan S. Chabay, Lloyd A. Currie, Alan Fried, Robert Gerlach, George A. Klouda, James E. Norris, Gerald B. Tompkins, Robert Continetti

4. Gas Metrology Group: Overview

The primary responsibility of the Gas Metrology Group continues to be the development and production of standard reference gases for all areas of science and technology where accuracy in gas measurement is required either by legislative mandate or necessity. Thus the group performs two major functions — the development of Standard Reference Materials (SRM's) and the performance of the research essential for the characterization of gas standards. In addition, a limited gas analysis service, utilizing the unique capabilities of the group, is provided to other groups at NBS and to other government agencies.

Research in the group has resulted in the development of high accuracy standards for the measurement of atmospheric concentration of nitrous oxide ($\sim$300 ppb). Development of standards for measurement of atmospheric concentrations of several halocarbons is progressing and work has begun on development of measurement techniques and standards for carbonyl sulfide, an important trace sulfur compound in the atmosphere.

A laser-diode spectroscopic technique has been developed to the point where comparative measurements of nitrous oxide can be made by this technique and gas chromatography using electron capture detection. The successful utilization of the two techniques is essential for the assessment of the accuracy of the nitrous oxide measurements. Standards for benzene and perchloroethylene at environmentally significant concentrations have been developed and their accuracy and stability have been studied. Standards consisting of both gas mixtures in cylinders and in permeation tubes have been evaluated.

Additional work has been done on high accuracy standards for measurement of atmospheric carbon dioxide. Final analysis of the potential SRM's will begin after delivery and evaluation of a state-of-the-art non-dispersive infrared analyzer.

As in the past, a major output of the group has been the analysis and certification of gaseous SRM's. Over 3,000 individual samples have been analyzed during the past year. In addition, 95 gaseous SRM's sold by the Office of Standard Reference Materials have been returned by users for reanalysis as part of a continuing study of stability. Four new SRM's have been issued during FY 81.

The development of the Certified Reference Material Program has been completed and CRM's are available from at least two commercial gas suppliers. The document outlining the program has been published in a joint NBS/EPA Special Publication. The current protocol describes the preparation of carbon monoxide in air or nitrogen, and nitric oxide in nitrogen CRM's. Documents concerning other gases are in preparation.

Service analyses performed by the group include an attempt to prepare and analyze samples containing ^{36}Ar and ^{40}Ar in an atmospheric matrix approximating that of the planet Venus. The mixture is needed to resolve a discrepancy between results of analyses made by investigations in the United States and Russia. The group continues to be involved in international evaluations of gas standards both through participation in international standards organizations and through cooperative analyses between various countries.

Future research plans of the Gas Metrology Group include: (1) continued research in laser infrared photometry as an accurate, sensitive analytical technique for gaseous molecules with large IR cross sections; (2) research on the theory and response characteristics of electron capture detectors used in gas chromatography; and (3) initiation of a new research effort in interfacial stability and surface enhanced reactions as they relate to gas mixture stability.

Ernest G. Hughes, Group Leader; William F. Cuthrell, William D. Dorko, James W. Elkins, Rudolph V. Kelly, Gerald D. Mitchell, Richard C. Myers, George C. Rhoderick, William P. Schmidt, Gerald A. Sleater, James E. Suddueth

5. Particle Research Group: Overview

The main objectives of the Particle Research Group are the development of particle generation techniques, and the characterization and improvement of particle measurement and collection techniques. Our research closely parallels some aspects of the Microanalytical Research Group efforts although our major emphases this year have been in the areas of particle sampling and *in-situ* measurement techniques.

A major accomplishment this year has been the completion of the design, construction, and complete wind tunnel testing and evaluation of the Personal Ambient Aerosol Sampler (PAAS). Two units of the PAAS have been sent to groups interested in evaluating it in field studies (the EPA and Harvard University School of Public Health). The work has been presented in whole or in part at three meetings during the year and we have already received requests for the papers describing the PAAS from both national and foreign environmental and occupational health scientists. The PAAS was designed and has been demonstrated to collect both the inhalable and the respirable fractions of particles from an air sample and to have a sampling cut-point (particle size discrimination) that follows that recommended by the AEC. It is wind-velocity and direction insensitive for indoor and mild outdoor conditions. The high sampling rate that has been achieved (6 L/min) has resulted in high interest by many researchers.

The group participated in an intercomparison study of several Aitken nuclei and cloud condensation nuclei counters during the International Cloud Condensation Nuclei Workshop (October 6-17, 1980, Reno, Nevada). A result of this work was the characterization and critical intercomparison and evaluation of the performance parameters of several Aitken counters which have been informally used as "standard" counters. This intercomparison has provided a clearer understanding of the conditions under which one may expect the particular instruments to measure Aitken nuclei concentrations accurately and of the subtle pitfalls that may be encountered in using these instruments naively.

A third effort this year has been the preparation and initial characterization of Min-U-Sil 5 as a candidate material for the production of a Respirable α-Quartz SRM. We have made particle size distribution studies of the material to verify that it is in the respirable range and are coordinating the other aspects of the certification measurements (including x-ray diffraction, infrared absorption, and thermogravimetry).

Finally, in collaboration with the Atmospheric Chemistry Research Group, we have made wind tunnel tests of air velocity and relative directional effects on the sampling efficiency and properties of gaseous pollutant personal samplers. We have developed gas generation and dispersion techniques for introducing sample gases into the tunnel and have characterized the resulting gas concentration profiles in the tunnel. We subsequently initiated a study of the sampling efficiency of the Palmes-tube NO_2 sampler as a function of wind speed and direction.

The Particle Research Group plans to initiate several new research areas next year in collaboration with other groups in the Division, the CAC, and the Center for Fire Research. These include: (1) development of particulates and thin films (of deposited particles) of known chemical composition as standards for microanalytical techniques; (2) characterization of the size and chemical distribution of particles resulting from spark discharge techniques for transport of materials from bulk samples to various plasma and flame spectroscopic analytical instruments; and (3) measurement of the formation and growth of gas or vapor/aerosol systems to test modeling experiments of smoke and related aerosol systems (i.e., the homogeneous and heterogeneous nucleation and subsequent growth of particles by condensation from the vapor phase).

Raymond L. McKenzie, Group Leader; David S. Bright, Robert A. Fletcher

B. Selected Technical Accomplishments (Gas and Particulate Science Division)

1. Development of a Monte Carlo Electron Trajectory Simulation

Monte Carlo electron trajectory simulation techniques have proven to be powerful tools for the study of electron interactions in solids [1]. Monte Carlo techniques have been applied to problems in scanning electron microscopy and electron x-ray microanalysis and, more recently, to the newly developed microanalytical method of analytical electron microscopy [1-3]. The Microanalysis Research Group has worked on the development and implementation of Monte Carlo techniques for microanalysis studies for several years [1,2,4,5]. During this time, frequent requests have been received from the microanalysis community for a Monte Carlo simulation which can be implemented by users on small laboratory computers. This year we have developed such a Monte Carlo simulation for distribution which incorporates a number of calculations of interest in microanalysis and we are making this computer program available to the community [6].

The simulation is of the single scattering type and is based upon the relativistic screened Rutherford elastic scattering cross section for the calculation of the mean free path between scattering sites and the elastic scattering angles. The Bethe continuous energy loss relation is used to account for inelastic scattering. The Bethe cross section for inner shell ionization is employed for x-ray calculations, with the constants in the cross section selectable among those due to Powell, Mott and Massey, Green and Cosslett, and others. The parameters calculated include the electron backscatter and transmission coefficients, the depth and lateral x-ray generation distributions, and the x-ray depth distribution corrected for absorption within the sample.

Two examples of x-ray distribution functions obtained by the Monte Carlo simulation technique are shown in figures 42 and 43. The variation of the shape of the depth-distribution curves can be interpreted in terms of the increased scattering power of the high atomic number targets. The simulation can be applied to the problem of examining interelement effects, particularly absorption, in thin foils. This scattering and absorption information is needed for the development of advanced quantitation methods for analytical electron microscopy.

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D. E. Newbury, R. L. Myklebust

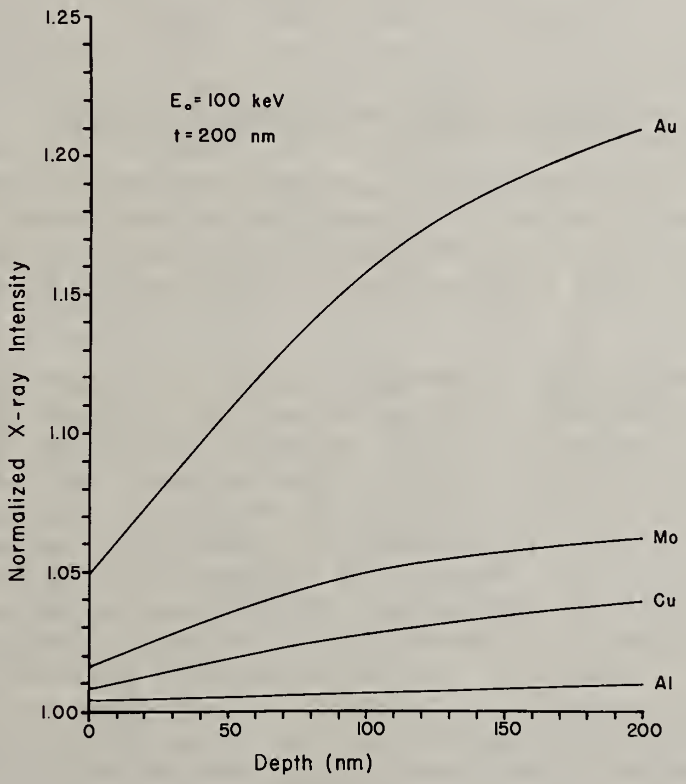

Figure 42. X-ray depth distribution functions for targets of various thicknesses.

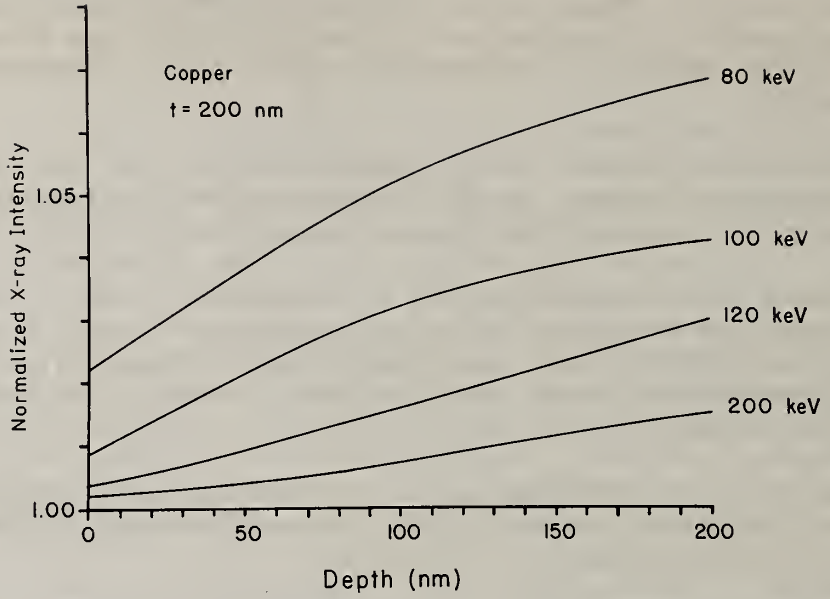

Figure 43. X-ray depth distribution functions for copper at various beam energies.

2. Empirical Quantitation in Raman Microprobe Analysis

Research has been initiated to quantitate micro-Raman scattering data from solid phase microsamples. The quantitative interpretation of the Raman spectra of microparticles is a difficult problem owing to the complexities of the underlying scattering phenomena and the difficulties of the experiment itself [1,2].

Theoretical treatments of inelastic scattering (Raman and fluorescence) theory [3] predict that the scattered intensities from microparticles are affected by (i) the geometrical (e.g., size and shape) and optical (e.g., refractive index) properties, (ii) the distribution of active molecules within the particle, (iii) the angular distribution of scattered light and polarization effects, and (iv) a number of instrumental factors. These same theories point out that the processes of inelastic scattering and optical absorption are closely related and postulate resonances in the Raman spectra of particles with perfect geometries (e.g., dielectric spheres and cylinders). Thus, while present theoretical understanding rests entirely on model calculations for isolated particles of perfect size and shape and ideal optical properties, an extension of these principles to particles that do not fit these models is not easily made and accounts for the lack of progress in quantitation.

We have evaluated the results of empirical approaches to quantitation and have assumed that, in a first approximation, the relationships for quantitation in macro-Raman spectroscopy [4] can be extended to micro-Raman scattering. That is, the scattered intensity from microscopic particles will be found to be proportional to the concentration of the species which generates the Raman band. Based on this premise, we have examined empirical quantitation by means of working curves, establishing detection sensitivities for inorganic species (and organic compounds) in simple solid matrices. The scattering systems investigated have ranged in optical/spectral complexity from samples transparent to the exciting radiation to solid phases nearly opaque to the incident laser beam. Observations to date suggest that the quantitative aspects of micro-Raman scattering may be tractable for a broad range of microsamples.

The solid phase matrix presently under intensive study is the carbonate-apatite system, of great relevance to biological mineralization [5,6]. In this area, our studies are directed at the determination of carbonate contents in vertebrate tissues of bone and tooth, work performed in collaboration with the American Dental Association Health Foundation, Research Unit at the NBS, and workers at the Children's Hospital Medical Center of Harvard Medical School.

The organic matrices of bone and dentin constitute approximately 30 percent of their respective dry weights. A solid inorganic mineral phase of which hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, in the final form contributes the remaining 70 percent dry weight. Bulk chemical analysis of mineralized tissue shows a carbonate (CO_3^{2-}) content varying with age from 1.4 percent to 6.2 percent in mature chick bone. The principal tissues examined are samples of bone and tooth, studied as powders and thin sections. To quantify the carbonate contents in these matrices, a series of synthetically prepared carbonate apatites have been obtained as standards, with CO_3^{2-} contents varying from ∿1.5 to ∿20 weight percent. The molecular groupings in these solids give rise to characteristic Raman bands. The bands with Raman shifts of ∿961 cm^{-1} (ν_1 mode, PO_4^{3-}) and ∿1074 cm^{-1} (ν_1, CO_3^{2-}) were selected as the analytical bands. Carbonate-to-phosphate intensity ratios were obtained from the spectra of these standards taking into account the spectral "background" at each analytical frequency. This procedure yields a calibration curve from which the composition of the mineral phase can be determined. Typical spectra from these studies are shown in figure 44. Comparison of the two spectra from mature chick bone and a 4.3 weight percent carbonate apatite standard indicates that the method of relative intensity measurements yields quantifiable data for this system. The calculated values for the CO_3^{2-}/PO_4^{3-} intensity ratio are 0.19 for both the bone sample and the carbonate apatite standard, after background corrections. The exact trend over the composition range of interest has not been fully established, although a linear relationship with concentration is indicated.

Future research efforts will have the objective of experimental verification of the predications made by the scattering theories for small particles. Also of importance will be the development and characterization of micro-Raman "standards" that have well-defined geometry, known composition, homogeneity, and are stable under laser irradiation. These data will then result in the development of the required empirical correction procedures.

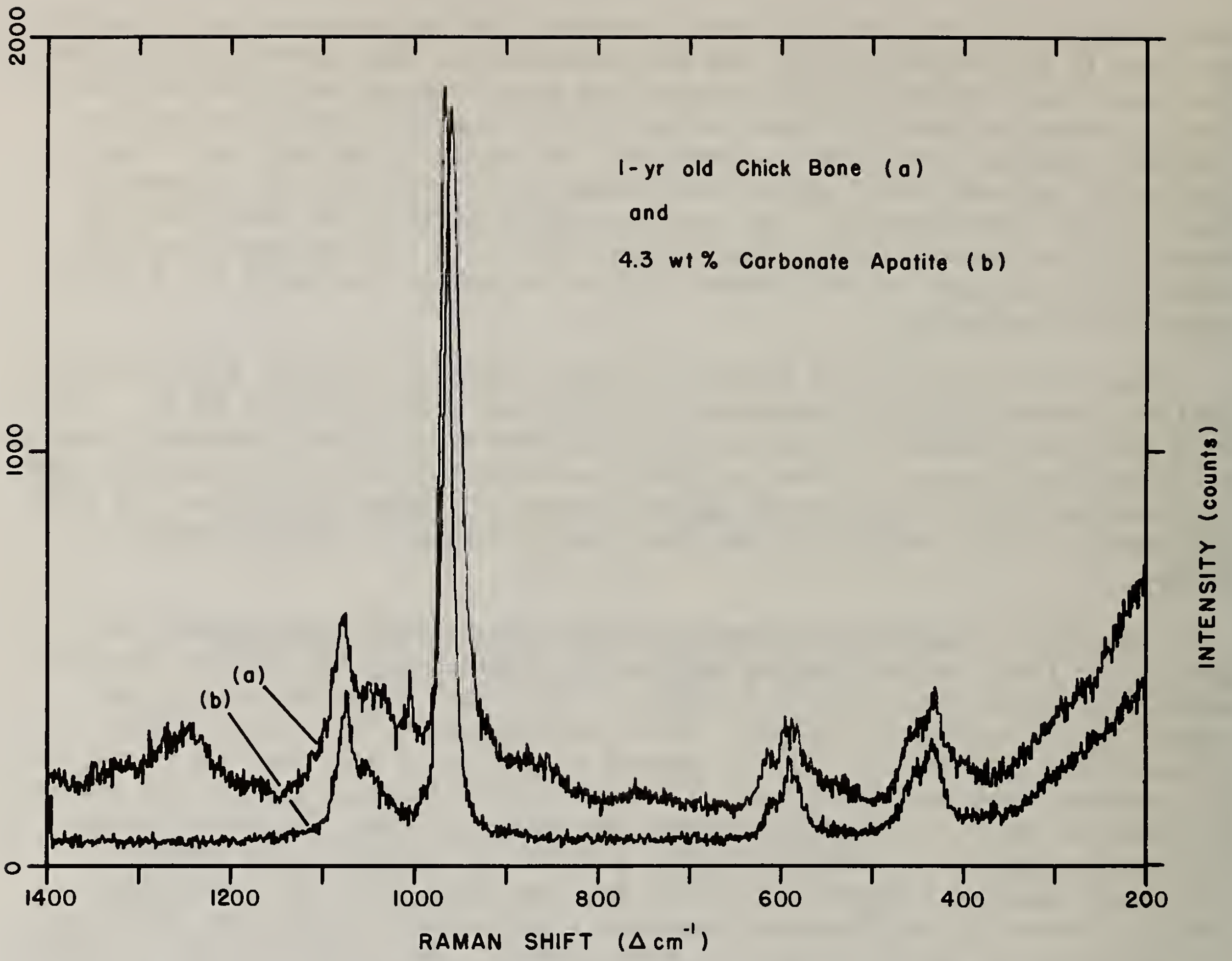

Figure 44. Raman microprobe spectra of single particles of (a) fully matured chick bone (powder) and (b) synthetic carbonate apatite.

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E. S. Etz

3. Automation of the NBS Laser-Raman Microprobe

The NBS laser-Raman microprobe has been automated to increase its research and analytical utility. A Digital Equipment Corporation MNC DecLab-11 system has been interfaced to the laser-Raman microprobe and now controls many of the instrument functions as well as data acquisition. The computer is a PDP-11/03 with 64 kilobytes of memory, dual 5 megabyte firm disks, and a CRT console. The console serves both as the computer terminal and as the display device for the spectral data. The computer is interfaced through a series of plug-in modules as is shown in figure 45. Two 16-bit digital input modules and three 16-bit digital output modules are used in this system. One output module controls the stepping motors on the spectrometer and the strip-chart drive motor as well as the Burleigh dual PZT translator stage to position the specimen. The output of the encoders on the spectrometer is read by the computer through an input module. The second input module reads the output from the SSR photon counter which is controlled by the second output module. The third output module controls the Houston Instruments Complot digital recorder. All signals in the system are digital and no amplification outside the SSR photon counter is required.

The software consists of two parts: the first part initializes all of the spectrometer functions, controls the system for data collection, and does the data acquisition. The second part controls all of the data display, consisting of the CRT graphics display and the digital plotter. Spectra may be displayed and compared on the CRT terminal. Hard copies of the spectra may be plotted on the digital plotter.

An important consequence of the automation of the system is the direct spectral digitization for our micro-Raman spectral library. Plans are for the future development of a file searching technique using peak location and band intensity data for matching reference spectra with the spectra of unknowns.

J. J. Blaha, E. S. Etz, R. L. Myklebust

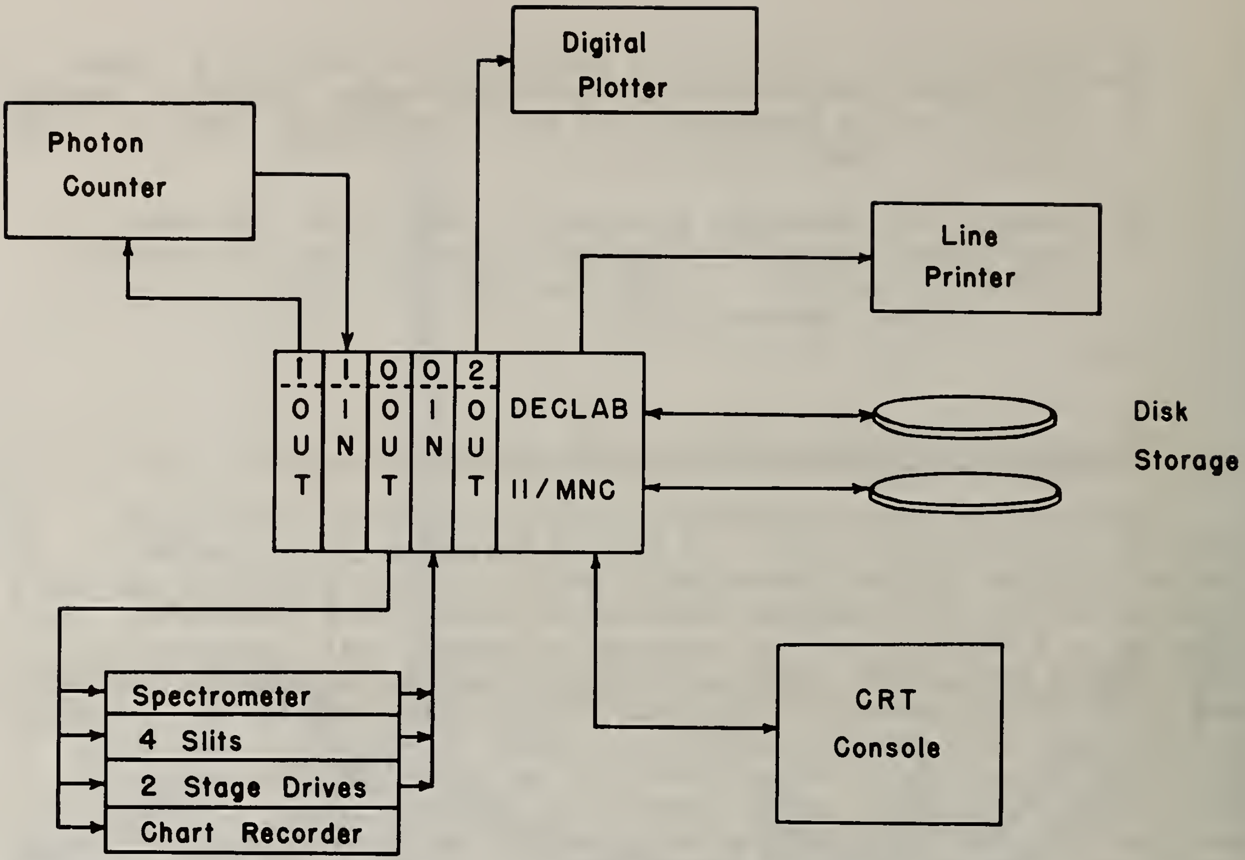

Figure 45. Schematic diagram of Laser-Raman microprobe data acquisition, processing, and output computer interface.

4. Development of Standards for Single Particle Analysis of Fly Ash

Fly ash from coal-fired power plants is one of the major sources of airborne particulate materials in the United States, accounting for approximately 25 percent of all anthropogenic particle emissions. The study of the environmental impact of fly ash is essential, as well as the study of its role as an industrial raw material.

Since the elemental composition of fly ash material varies from particle to particle, it is necessary to quantitatively analyze individual fly ash particles by microanalytical techniques as part of the total characterization of the material. These individual analyses are then statistically grouped and compared to bulk composition. The development of methods for and the analyses of individual particles is dependent on developing well characterized particle standards.

During the past several years the Microanalysis Group has been involved in a cooperative program with the Inorganic Glass Group (Center for Materials Research) to develop microanalytical measurement standards.

As part of this program, we have developed a surrogate fly ash consisting of glass microspheres ranging from 0.5 µm to 250 µm in diameter. The microspheres are prepared by pumping an air suspension of finely ground glass through a vertically mounted alumina tube. The tube is heated to the melting point of the glass and the irregular particles are drawn into a special shape by surface tension. After formation, the microspheres are air cooled and collected on polycarbonate filters (figure 46).

Figure 46. Glass microspheres synthesized in forced draft furnace.

The composition of the parent glass used in the manufacture of the synthetic fly ash is given in Table 29. This composition was selected to simulate the elemental concentrations found in many types of fly ash particles.

In order to determine if there were any alterations in composition of the microspheres as a result of the preparative (production) process, the composition of the microspheres was compared to the bulk glass. For this comparison the microspheres were cross-sectioned to minimize particle absorption, and polished to an optically flat surface. Table 30 lists the elemental ratios for microspheres compared to bulk glass for 60 analyses on 15 cross-sections. The ratios for all the elements are close to, but slightly less than unity. This discrepancy can be attributed to a particle mass effect which is the loss of x-ray intensity from the microspheres as a result of electrons penetrating through the microspheres into the epoxy.

Table 29. Partial Compositions of Bulk Glass K-961.

Element	Weight Fraction K-961[a]
O	0.470
Na	0.030
Mg	0.030
Al	0.058
Si	0.299
P[b]	0.002
K	0.025
Ti	0.012
Ca	0.036
Mn[b]	0.003
Fe	0.035

---

[a] Composition based on constituents used to make the bulk glass.

[b] For K-961 the elements phosphorus and manganese were not analyzed because of the low amounts of these elements in the glass.

Table 30. Average Intensity Ratios to Bulk Glass for K-961 Microspheres.

Element	Average	Standard Deviation	Standard Deviation of a Single Determination	Poissonian Standard Deviation of a Single Determination
Na	0.97	0.004	0.18	0.049
Mg	0.96	0.001	0.050	0.025
Al	0.96	0.0009	0.041	0.014
Si	0.98	0.0005	0.025	0.006
K	0.97	0.0009	0.039	0.019
Ca[a]	0.98	0.0009	0.033	0.017
Ti	0.98	0.0009	0.042	0.026
Fe	0.93	0.0009	0.042	0.026

---

[a] The potassium K_β peak has been subtracted.

The results from the analyses of the microspheres indicate that, within the uncertainties of the techniques used for sample preparation and analysis, there is no alteration in composition due to the preparative process. These microspheres are serving two important functions. First they are being used as direct standards for semi-quantitative electron probe analysis of fly ash particles. Secondly the spheres are being used to develop a general analytical correction procedure for the quantitative electron microprobe analyses of individual particles.

J. A. Small

5. Development of a Candidate Thin Film Standard Reference Material

The development of advanced high spatial resolution analytical techniques such as analytical electron microscopy (AEM) and laser microprobe mass analysis (LAMMA) which require samples in the form of thin films has placed new demands on standards development. Standards of known composition are now required which are laterally homogeneous on a scale of nanometers and which have a known and constant thickness on the order of 100 nm. To supply these standards, we have investigated ion beam sputtering of glass targets to produce films with suitable, constant properties [1]. Ion beam sputtering has been previously utilized by the X-Ray Fluorescence Group to produce thin film standards on filter material. For the new work, it has been necessary to extend the procedure to produce standards which can be demonstrated to be stable and homogeneous on a submicrometer spatial scale. A schematic of the apparatus for the production of the films is shown in figure 47. The glass target is sputtered with a beam of 1 keV Ar^+ ions, and the sputtered material is deposited on thin (20 nm) carbon films carried on copper or beryllium grids. To improve the homogeneity, the substrates are mechanically rotated relative to the source during glass deposition.

The initial test film which was produced had the nominal composition of NBS SRM K-411 glass [MgO (15 wt. %); SiO_2 (55 wt. %); CaO (15 wt. %); FeO (15 wt. %)]. Contaminants in the commercial sputtering apparatus used introduced aluminum and chlorine into the films, although this problem has been eliminated in subsequent runs. Homogeneity was determined by electron probe analysis with energy dispersive x-ray spectrometry. Figure 48 shows the results for the ratio of iron to calcium. In this figure, the box represents the range for 50 percent of the analyses, and the bars show the maximum excursions. The standard deviations for the ratios of the various elements to calcium were in the range ±3 percent relative. Moreover, this includes even the chlorine contaminant, indicating the strong bonding formed during the sputtering process. Thickness measurements by double-beam interferometry and stylus profilometry revealed a constant thickness within ±20 percent relative.

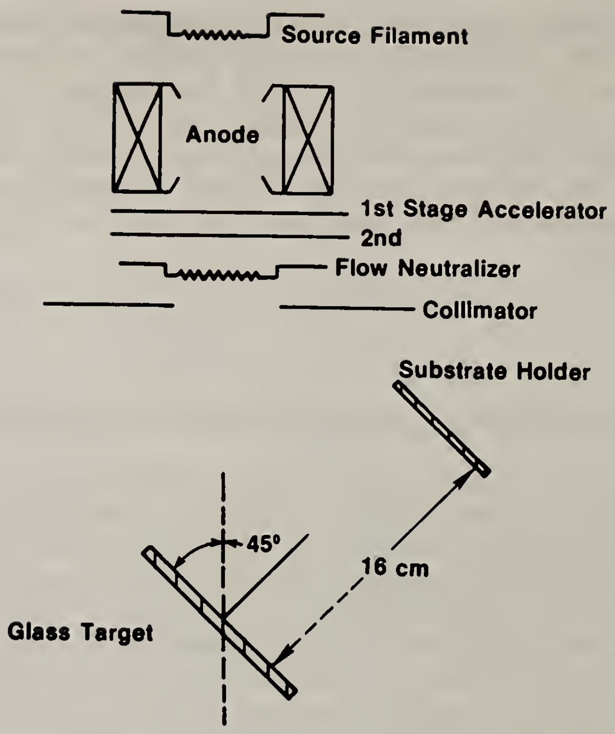

Figure 47. Schematic of the ion sputtering apparatus.

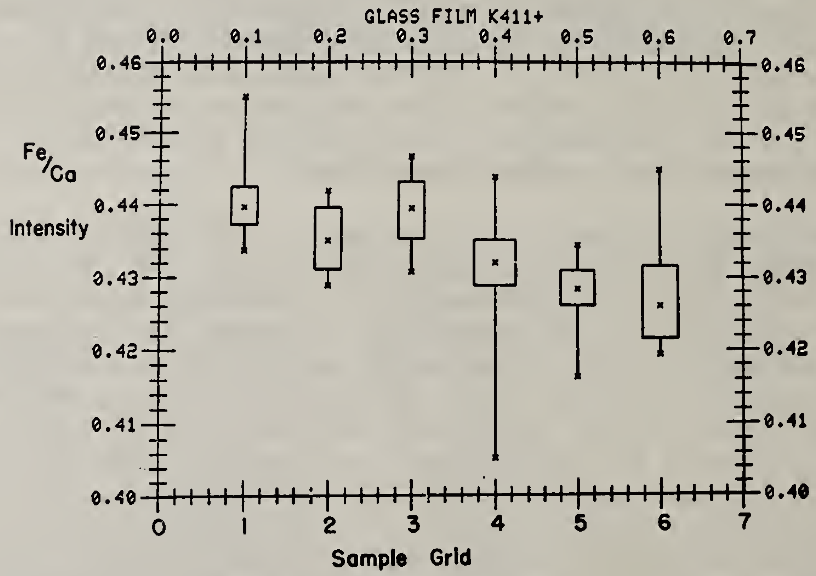

Figure 48. Diagram showing the variability in ratio of Fe to Ca x-ray intensities for six samples analyzed on the electron microprobe.

The results obtained so far on the homogeneity and stability of the candidate materials suggests an excellent basis exists for the development of a thin film standard reference material. Because sputtering does not necessarily transfer the target composition faithfully to the film, it will be necessary to analyze the sputtered films by independent techniques such as neutron activation and atomic absorption.

Reference

[1] Steel, E. B.; Newbury, D. E.; Pella, P. A. "Preparation of Thin Film Glass Standards for Analytical Electron Microscopy" to be published in Proc. 3rd Workshop on Analytical Electron Microscopy.

E. B. Steel, D. E. Newbury, P. A. Pella

6. Intercomparison of NRLXRF Semi-Empirical and NBS Interelement Correction Methods

Proper corrections for interelement effects in quantitative x-ray fluorescence spectrometry are a major factor in obtaining accurate compositional data. Various semi-empirical approaches to obtaining correction factors have been published. A widely used approach which combines the use of influence coefficients and fundamental parameters was developed by the Naval Research Laboratory. This program, called NRLXRF [1], allows the user to select from three analysis schemes. These are called "Empirical", "Full", and "Theoretical" and their selection will depend upon which standards are available. The purpose of the NBS work was to compare the results obtained with each of the three options in NRLXRF and to check for consistency in the results by intercomparison with another semi-empirical model such as Rasberry-Heinrich [2] and an NBS fundamental parameter method EXFNBS [3]. The samples chosen for the intercomparison consisted of a series of well-characterized alloys analyzed for Fe, Ni, and Cr.

The results obtained with the Rasberry-Heinrich method and the Empirical option of NRLXRF are summarized in Table 31. The Empirical option of NRLXRF uses a form of the Lachance-Traill equation and a weighted least-squares procedure which emphasizes the standards whose composition are most like the unknown specimens. Comparison of the results in Table 31 indicate that these procedures are comparable for samples 5054, 5364, and 5202 where the relative error is 1.1 to 1.5 percent. These procedures give optimum results when the total composition of the analyte is determined or accounted for as in the case of the ternaries where the sum of the constituents equal 98 percent or better. For alloys like NBS-SRM 1188, however, 5 percent of the total elemental composition consists of the elements Ti, Al, Si, and Nb. If this sample is treated as a ternary only, the relative error increases to 3-3.5 percent, as shown in the table. The Empirical option in NRLXRF contains a provision for adjusting the weight fractions of the analytes for the presence of known concentrations of elements in the unknown specimen. Entering the known weight fractions of Ti, Al, Si, and Nb for 1188 and then treating the sample as a ternary reduces the relative error to 1.2 percent. Similar improvements in the results could be made with the Rasberry-Heinrich method if influence coefficients are included in the analysis scheme for Ti, Al, Si, and Nb.

Table 31. Comparison of Rasberry-Heinrich and NRLXRF (Empirical Option).
(all concentrations are in weight percent)

Specimen I.D.	Chem.	R-H[a]	R.E.[d]	R-H[b]	R.E.[d]	Emp.[c]	R.E.[d]
			Iron				
5054	72.50	72.29	-0.29	72.71	0.29	73.07	0.79
5364	47.21	47.50	0.61	47.56	0.74	47.32	0.23
5202	63.03	62.77	-0.41	62.84	-0.30	62.96	-0.11
1188[e]	6.60	6.55	-0.76	6.05	-8.3	6.21	-5.9
1188[f]	6.60	-	-	-	-	6.74	2.1
			Nickel				
5054	0.150	0.15	0.0	0.16	6.7	0.16	6.7
5364	23.57	24.09	2.2	23.71	0.59	23.68	0.47
5202	14.80	15.07	1.8	14.73	-0.47	14.78	-0.14
1188[e]	72.65	72.36	-0.4	72.11	-0.74	73.98	1.8
1188[f]	72.65	-	-	-	-	72.88	0.3
			Chromium				
5054	25.77	25.22	2.13	26.00	0.89	25.38	-1.5
5364	27.84	26.75	3.9	27.49	-1.3	27.78	-0.22
5202	21.30	20.90	1.9	21.17	-0.61	21.27	-0.14
1188[e]	15.40	14.21	-7.7	15.36	-0.26	14.95	-2.9
1188[f]	15.40	-	-	-	-	15.21	-1.2

Data Summary, Average Relative Error in Percent

Specimens			
5054, 5364, 5202	1.5	1.3	1.1
1188[e]	3.0	3.1	3.5
1188[f]	-	-	1.2

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[a] R-H = data from Rasberry and Heinrich [3].

[b] R-H = this work (Cr target 50 kV, 10 mA, and $\beta_{FeNi} = -0.70$).

[c] Emp. = NRLXRF (empirical option).

[d] R.E. = Relative error, percent = $\frac{\text{OBS. VALUE-CHEM. VALUE}}{\text{CHEM. VALUE}} \times 100$.

[e] 1188 = Treated as a ternary and analyzed for Fe, Cr, and Ni only.

[f] 1188 = Analyzed for Fe, Ni, and Cr, however, the known concentrations of the unanalyzed elements were included.

The results of analyses on the same set of standards for the NRLXRF Full and Theoretical options and EXFNBS are presented in Table 32. These results are also consistent with those presented in Table 31 where the average relative error was 1.3-1.5 percent. Using only pure element standards for calibration (i.e., Theoretical option in NRLXRF), the relative errors were 3.6 percent for NRLXRF and 2.2 percent for EXFNBS. The slightly better values obtained with EXFNBS are probably due to the use of a very efficient exciter (e.g., Zn) for Fe, Ni, and Cr in which case the effect of secondary and tertiary fluorescence effects are minimized.

References

[1] Birks, L. S.; Gilfrich, J. V.; Criss, J. W. "NRLXRF, a FORTRAN Program for X-Ray Fluorescence Analysis," X-Ray Optics Branch, Material Sciences Division, Naval Research Lab., Washington, D. C. 1977. (COSMIC) Suite 112, Barrow Hall, Athens, Georgia 30602, Prog. No. DOD-00065, (July 1977 version).

[2] Rasberry, S. D.; Heinrich, K. F. J. Anal. Chem. 46: 81; 1974.

[3] Myklebust, R. L.; Pella, P. A.; Thorne, B. (to be published in X-Ray Spectrom).

P. A. Pella, J. R. Sieber

Table 32. Analysis with NRLXRF and EXFNBS
(all concentrations are in weight percent)

Specimen I.D.	NRLXRF					EXFNBS			
	Chem.	Full[a]	%R.E.	Theo.[b]	%R.E.	All Stds.[c]	%R.E.	El. Stds.[d]	%R.E.
					Iron				
5054	72.50	71.86	-0.88	73.77	-1.75	73.04	-0.74	72.57	-0.09
5364	47.21	47.68	+1.0	47.02	0.40	47.26	-0.11	47.00	0.44
5202	63.03	62.91	-0.19	62.39	1.02	63.48	-0.71	63.04	-0.02
1188	6.60	6.81	+3.18	6.97	-5.61	6.69	-1.36	6.68	-1.21
					Nickel				
5054	0.150	0.16	+6.7	0.170	-13.3	0.145	3.33	0.146	2.7
5364	23.57	23.67	+0.42	25.14	-6.7	23.90	-1.40	23.95	-1.61
5202	14.80	14.71	-0.61	15.84	-7.0	15.05	-1.69	15.08	-1.89
1188	72.65	72.22	-0.59	72.05	0.83	73.49	-1.16	73.65	-1.38
					Chromium				
5054	25.77	25.71	-0.23	26.05	-1.09	25.57	0.78	26.56	-3.07
5364	27.84	27.93	+0.32	27.84	0	28.22	-1.36	29.17	-4.78
5202	21.30	21.48	+0.85	21.77	-2.21	21.70	-1.88	22.44	-5.35
1188	15.40	15.81	+2.66	15.81	-2.66	15.57	-1.10	16.04	-4.16
Average relative error, %			1.5		3.55		1.30		2.23

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[a] Full option using all ternary standards plus SRM 1189.

[b] Theoretical option using pure elements only for calibration.

[c] All ternary standards plus SRM 1189 used.

[d] Pure elements only used for calibration.

7. Measurement of the Temperature Dependence of the Ozone Absorption Cross-Sections in the Ultraviolet

Work has continued on the determination of temperature dependence of the ozone ultraviolet absorption cross-sections. The ultraviolet photometer was described in last years report to the panel and is functioning as planned.

The goal of this project is to determine the ozone cross-sections over a range of wavelengths and temperatures that are of particular concern in stratospheric measurements and modeling. Thus we propose to record the spectrum over the wavelength range 200 to 700 nm and over the range of temperatures 200 to 300 K. We have now completed measurements over the region of the Hartley and Huggins Bands (240 to 340 nm) at two temperatures (298 K and 243 K). These measurements have been made in steps of 0.05 nm with a spectral resolution of approximately 0.02 nm. Several scans were made of this region of the spectrum. The consistency of the determinations between repeated scans was very good. The uncertainty of the measured cross-sections, relative to the cross-section at 254 nm, is estimated to be less than 2 percent.

Figure 49 displays the absorption spectrum between 345 and 260 nm. The upper curve is for 295 K; the lower curve is for 243 K. Figure 50 shows the region between 345 and 325 nm in greater detail. In both cases the plotted curves represent the average of at least three individual scans through the spectral range quoted.

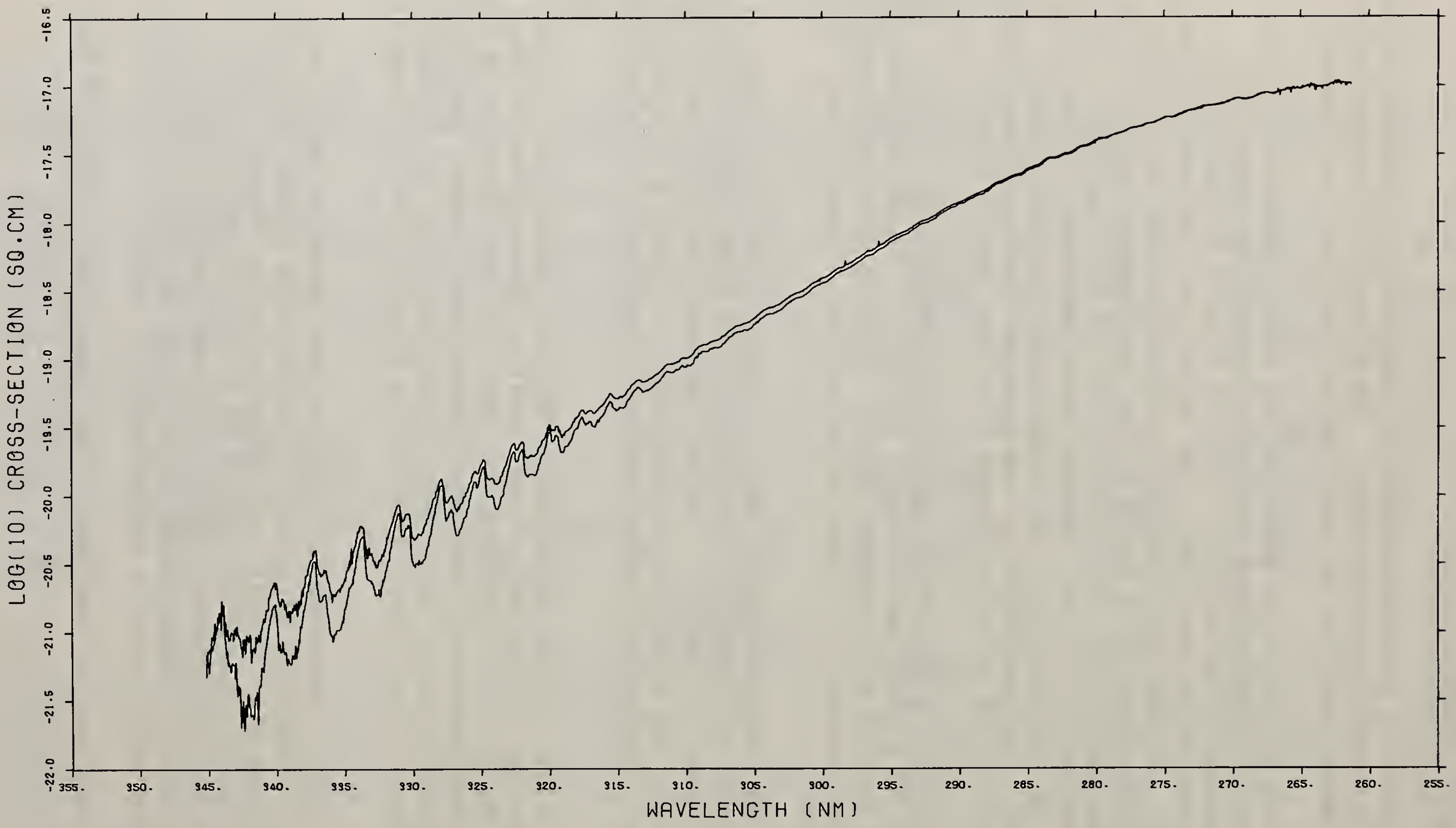
The ratio of the cross-section at 243 K to that at 298 K is plotted as a function of wavelength in figure 51. The ratio values published previously by Vigroux are indicated by the x's. The real and detailed structure of the temperature coefficient as a function of wavelength is clealy displayed in contrast to the very limited information previously available in the published literature.

The value of these improved measurements has been demonstrated by two research groups involved in the analysis of satellite observations of ozone concentrations in the Earth's atmosphere. In one case, discrepancies of about 3.5 percent which were previously observed in comparisons between satellite and ground-based measurements of ozone total column densities and of vertical profiles were reduced to less than 1.5 percent by using the new cross-section values.

In the second case, observation of backscattered radiation made from Nimbus 7 displayed unidentified structure in the spectrum between 280 and 310 nm. This structure was initially attributed to sulfur dioxide (SO_2) and implied a concentration of SO_2 of 200 ppb at 10 to 30 km, strongly in conflict by four orders of magnitude with *in situ* measurements. By using our new ozone cross-section measurements it was shown that essentially all of the spectral structure can now be accounted for by ozone.

We expect to complete the remainder of the measurements during FY 82.

A. M. Bass



OZONE ABSORPTION CROSS-SECTIONS

UPPER SPECTRUM 300K

LOWER SPECTRUM 243K

Figure 49. Ultraviolet absorption cross-section of ozone as a function of temperature:
Upper curve 298 K Lower curve 243 K.

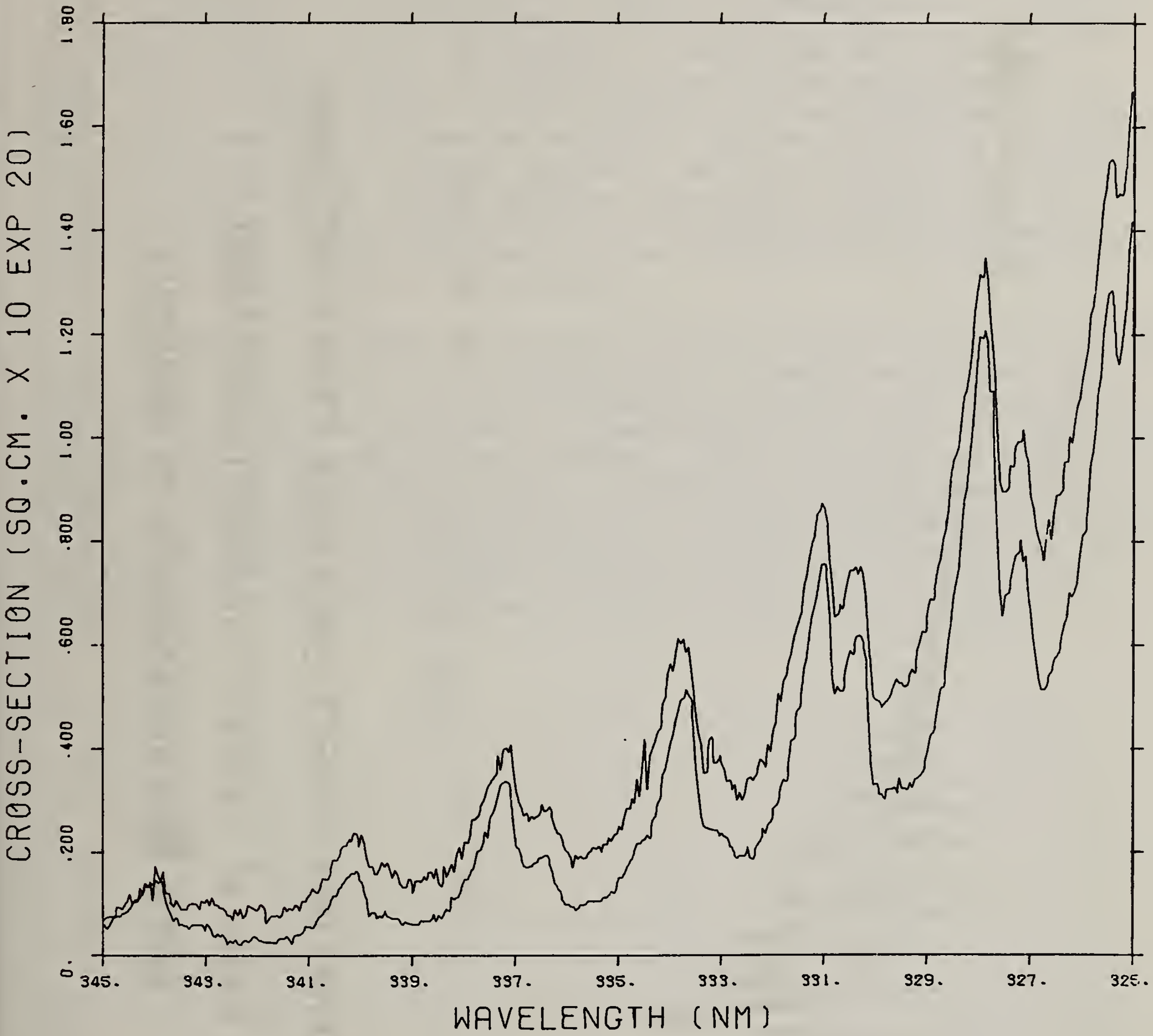
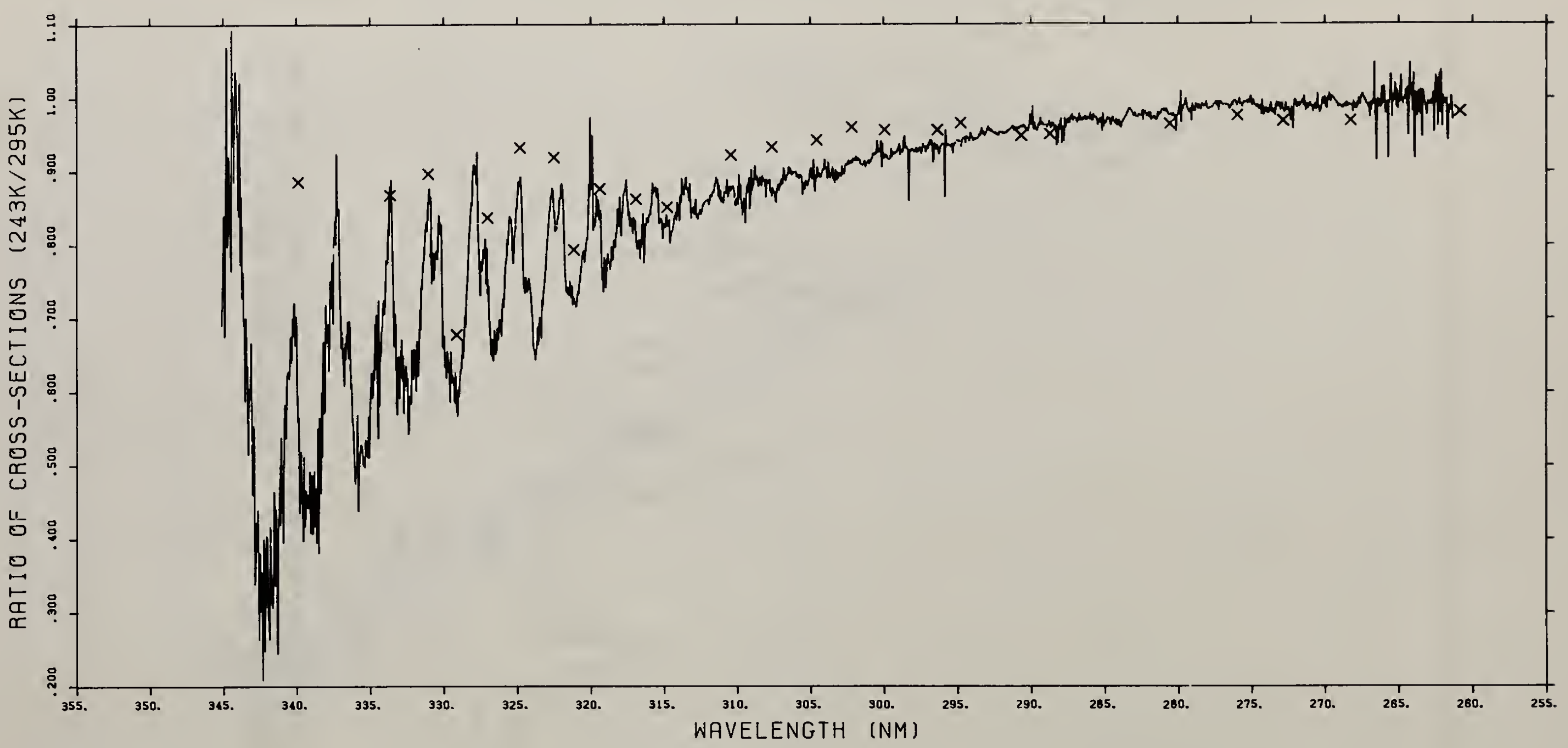


Figure 50. Ozone absorption in cross-section between 345 and 325 nm.
Upper curve 298 K Lower curve 243 K



TEMPERATURE EFFECT ON OZONE CROSS-SECTIONS
(ratio of $\sigma(243):\sigma(300)$) COMPARED
WITH MEASUREMENTS OF VIGROUX

Figure 51. Ratio of cross-sections at 243 K to those at 298 K. Earlier measurements by Vigroux are marked x.

8. Measurement of Infrared Intensities of Atmospheric Species

Over the last several years there have been increased efforts in the atmospheric science community to model the atmosphere. The goal is to obtain accurate measurements of both concentration profiles of most atmospheric constituents, and the temperature profile of the atmosphere. The purpose of these measurements is to predict the response of the ozone layer to changes in concentrations of other constituents, to understand the role of the atmosphere's composition as it effects climate, and to monitor pollution. Many of these studies employ infrared techniques to make atmospheric measurements, and therefore must rely on laboratory measurements of band intensities and line parameters to interpret the data. We have a program, in collaboration with personnel of the NBS Molecular Spectroscopy Division (CCP) to provide accurate infrared band intensity and line parameter measurements to fulfill the needs of the atmospheric science community and also to provide data for the preparation of gas standards.

For these measurements we employed a Fourier transform infrared spectrometer (FT-IR) with 0.01 cm^{-1} resolution for band strength measurements and a diode laser spectrometer (DLS) with $\sim$0.003 cm^{-1} resolution for line parameter measurements. We made three series of measurements with the FT-IR specifically to calibrate it for intensity measurements. These are the NO fundamental band, the N_2O ν_1 band and the OCS ν_1 band. In Table 33, our values are compared to values obtained by DSL and by a conventional grating spectrometer in the case of NO. The agreement in all three cases is to within a few percent and well within the estimated uncertainties of the comparison values. From this comparison we estimate the systematic error to be less than 5 percent.

Table 33. Comparison of FT-IR Band Strength Measurements with Literature Values.

Band System	NBS FT-IR Value for Band Strength, S of 296 °K (cm^{-2} atm^{-1})	Comparison Value, S of 296 °K (cm^{-2} atm^{-1})	References for Comparison Values
N_2O ν_1	224.9 ± 1.6[a]	219 ± 11[b] (DSL)	A. G. Maki and R. H. Kagann to be published
OCS ν_1	35.49 ± 0.80	35.4 ± 1.6 (DSL)	V. M. Devi, P. P. Das, A. Bano, and K. M. Rao J. Mol. Spec. <u>87</u>, 578 (1981).
NO $\nu = 1 \leftarrow 0$	113.6 ± 1.2	112 ± 6 (Grating)	L. L. Abels and J. H. Shaw J. Mol. Spec. <u>20</u>, 11 (1966).

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[a] The uncertainties listed in this column are 95% confidence limits (using student ± distribution) on the random error (the scatter in the Beer's law plot). The systematic error is not included here but is estimated not to exceed ∿5%.

[b] The uncertainties listed in this column include a contribution from the estimated systematic error.

After calibrating our FT-IR, we measured selected band strengths of the following atmospheric species: N_2O, NO_2, OCS, HNO_2, and N_2O_3. The results of these measurements are shown in Table 34. The uncertainties include contributions from the estimated systematic error of 5 percent and from random error in the data. The measurements of HNO_2 and N_2O_3 were made in equilibrium systems where both species were minor components. No direct measurements of the partial pressures were possible, so the pressures were calculated using literature values for the appropriate equilibrium constants. This and the fact that the two species were present in the equilibrium mixtures in small concentrations (∿0.5 torr for HNO_2 and 0.1 torr for N_2O_3) account for the high uncertainties in the measurement of these two species. These are the first known measurements of infrared absorption intensities of HNO_2 and N_2O_3.

The data from the NO_2 measurements are presently being analyzed and we have just begun measurements of Freon 11 and plan to make measurements of Freon 12.

R. H. Kagann

Table 34. FT-IR Measurements of Band Strengths and Band Positions.

Band System		Band Center (cm^{-1})	Band Strength, S at 296 K (cm^{-2} atm^{-1})
NO	1→0	1876	113.6 ± 5.8
N_2O	ν_2^1	589	28.9 ± 1.5
	$2\nu_2^0$	1168	8.28 ± 0.46
	ν_1	1285	225 ± 11
	$3\nu_2^1$, Q	1749	0.0235 ± 0.0088
	$\nu_1+\nu_2^1$,Q	1880	0.254 ± 0.015
	$\nu_1+\nu_2^1$, system	1880	0.583 ± 0.085
	$\nu_1+2\nu_2^2-\nu_2$, Q	1886	0.0348 ± 0.0059
	ν_3	2224	1421 ± 92
	$\nu_1+2\nu_0^0$	2462	7.32 ± 0.39
	$2\nu_1$	2563	32.1 ± 1.7
	$\nu_2^1+\nu_3$	2798	2.25 ± 0.21
	$2\nu_2^0+\nu_3$	3364	2.21 ± 0.19
	$\nu_1+\nu_3$	3481	46.8 ± 2.5
	$2\nu_1+2\nu_2$	3749	0.702 ± 0.093
	$3\nu_1$	3836	1.86 ± 0.67
	$2\nu_3$	4417	1.53 ± 0.37

Table 34 continued.

Band System		Band Center (cm^{-1})	Band Strength, S at 296 K (cm^{-2} atm^{-1})	
OCS	ν_1	858	35.5	± 1.9
	$2\nu_2$	1044	13.35	± 0.78
	$2\nu_1$	1711	6.71	± 0.44
	$\nu_{+}{}^{+2}\ {}_{2}$	1893	10.91	± 0.69
	ν_3	2062	2984	± 177
	$\nu_2+\nu_3$,Q	2575	0.0596	± 0.0064
	$\nu_1+\nu_3$	2918	33.6	± 1.9
	$2\nu_2+\nu_3$	3095	2.26	± 0.14
	$2\nu_3$	4102	17.9	± 1.7
CIS-HNO_2	ν_4	852	960	± 140
	ν_2	1640	1250	± 240
	$2\nu_2$	3257	30	± 5
	ν_1	3427	69	± 20
Trans-HNO_2	ν_4	790	563	± 82
	ν_3	1263	699	± 86
	ν_2	1699	704	± 81
	($2\nu_3$ or $\nu_2+\nu_4$?)	2493	25	± 6
	$2\nu_2$	3372	37	± 6
	ν_1	3590	246	± 29
N_2O_3	ν_1	1302	1180	± 180
	ν_1	1829	1302	± 180

9. Continuation of the Intercomparison of O_3, NO, and NO_2 Measurement Standards by Gas Phase Titration

In our research summary presented last year, intercomparison of ozone (O_3), nitric oxide (NO), and nitrogen dioxide (NO_2) measurement standards using the rapid bimolecular reaction

$$NO(excess) + O_3 = NO_2 + O_2,$$

was discussed in detail. In these studies, NO was titrated by incremental additions of O_3. The concentration of NO reacted, $\Delta(NO)$ as measured by chemiluminescence and calibrated by NO Standard Reference Material (SRM) cylinders, was compared with UV photometric measurements of the O_3 concentration added, $\Delta(O_3)$. Preliminary measurements of the NO_2 concentration generated during the course of this reaction, $\Delta(NO_2)$, were also made. This was accomplished utilizing an NO_2 optoacoustic detection system calibrated by permeation tube standards. In this method of detection, NO_2 is measured directly without an interfering response from NO, thus eliminating considerable measurement uncertainty inherent in the more traditional chemiluminescent measurements of NO_2. The data obtained from the three independent measurements revealed excellent agreement between the $\Delta(NO)$ and the $\Delta(NO_2)$ concentrations determinations, while the $\Delta(O_3)$ concentration values averaged 3 to 4 percent lower.

During the past year we have continued the study of these intercomparisons. A more extensive set of $\Delta(NO)$, $\Delta(NO_2)$, and $\Delta(O_3)$ measurements confirm our previously reported results. These data were fitted using a linear regression. However, since the uncertainties in all three determinations are comparable in magnitude, a weighted regression was employed using an iterative technique described by Derek York; the residuals in both the ordinate and abscissa were simultaneously minimized, in contrast to ordinary least-squares data treatment. The following relations were thus generated:

$\Delta(O_3)_{uv}$ ppm = $[0.964 \pm 0.005]\ \Delta(NO)_{grav.} - [0.003 \pm 0.004]$, (56 data pairs)

$\Delta(NO_2)_{perm.\ tube}$ ppm = $[1.006 \pm 0.007]\ \Delta(NO)_{grav.} - [0.004 \pm 0.005]$,

(22 data pairs.

The agreement between $\Delta(NO)$ and $\Delta(NO_2)$ verifies the reaction stoichiometry.

In an attempt to identify the source of the 3.6 percent bias found in the $(O_3)_{uv}$ measurements, other reactions have been considered which cause the oxidation of NO to NO_2 without consuming O_3. The most obvious,

$$2\ NO + O_2 \rightarrow 2\ NO_2,$$

accounts for only approximately 0.2 percent, as both measured and calculated in this study. An alternative set of reactions also considered involves the chemistry of impurities in the "clean air" source used in the generation of

O_3. Impurities such as N_2O, CH_4, CO, and CO_2 have been measured at ambient concentrations. In addition, water vapor concentrations ranging from approximately 10 ppm to a few hundred ppm have also been measured. The chemistry of these impurities centers around the production of the OH radical in the O_3 generator which subsequently generates CH_3O_2 and HO_2 radicals, both of which are known to react very rapidly with NO to produce NO_2. Fourty-seven reactions involving these impurities were studied by computer modeling our gas phase titration (GPT) experiments using typical flow and concentration conditions. Details of this model will be described in the following research summary. The computer routine used in this analysis was developed by Robert Brown of the Center for Chemical Physics. At the relative humidities measured in these experiments, the results from the modeling indicate a maximum increase in ΔNO relative to ΔO_3 on the order of a few tenths of one percent, much too low to account for the observed discrepancy of 3.6 percent. Relative humidities as high as 50 percent would be required to generate a 2 percent discrepancy in these species. We are, however, continuing to study the air stream source for, as of yet, undetected impurities which may effect the oxidation of NO to NO_2. We have also found that those species known to be present in the air source, as well as those reactive and stable end products predicted by the model, are not major interferences in the UV absorption measurements of O_3 at 253.7 nm.

In addition to the chemistry of impurities just described, we were also concerned about trace impurities in the air stream reacting directly with O_3, which because of the split flow stream arrangement could potentially yield lower O_3 concentrations during measurement. A series of GPT experiments were therefore carried out using a different flow scheme. The O_3 source, reaction, and mixing chambers were replaced by two larger glass vessels, a 1-liter reactor followed by a 2-liter mixing chamber. Ozone was introduced into the system by passing the ozonized air stream from the NBS 3-meter UV photometer directly into the reaction chamber. Not only did we eliminate the split flow stream in this manner, but it also enabled us to make simultaneous O_3 and NO measurements, thus eliminating a possible source of error due to lamp fluctuations in the O_3 source during the time between titration and O_3 measurement. This arrangement also enabled us to eliminate the necessity of the Dasibi transfer standard along with questions concerning the use of a different air source in the calibration and GPT phases. The results of these experiments using high purity air with water vapor concentrations less than 3 ppm and total hydrocarbon concentrations as CH_4 less than 0.1 ppm are very similar to previous GPT runs; the ΔNO concentrations as measured by chemiluminescence and calibrated by gravimetrically prepared standards ranged from 3 to 5 percent higher than the corresponding ΔO_3 concentrations as measured by UV photometry.

In future studies, we will continue to investigate air stream impurities by computer modeling, gas chromatography, and long path Fourier Transform Infrared Spectroscopy. This last technique will also be used in conjunction with a new and improved UV photometer to measure O_3 concentrations in gas phase titrations.

A. Fried, J. A. Hodgeson

10. Studies of the Photochemistry of Trace Airstream Impurities in Ozone Generators

In our studies intercomparing measurement standards by gas phase titration (GPT), we became concerned with chemical reactions that potentially could effect the oxidation of NO to NO_2 without consuming O_3 and hence account for the observed stoichiometry:

$$\Delta NO = \Delta NO_2 > \Delta O_3$$

In these studies, O_3 was produced by a conventional photolytic generator in which O_2 flowing through a quartz tube was photolyzed by UV radiation from a low pressure mercury lamp in accordance with the following reactions:

$$O_2 + h\nu\ (\lambda < 2424\ \mathring{A}) = 2\ O(^3p) \quad (1)$$

$$O(^3p) + O_2 + M = O_3 + M,\ M = N_2,\ O_2 \quad (2)$$

$$O_3 + h\nu\ (\lambda < 4000\ \mathring{A}) = O(^1D) + O_2 \quad (3)$$

In the absence of impurities in the O_3 generator airstream, reaction (3), the photolysis of O_3 in the generator, will simply regenerate O_3. However, impurities such as N_2O, CH_4, CO, CO_2 at ambient concentrations and H_2O vapor ranging from 10 ppm to a few hundred ppm have been measured in cylinder air used in the generation of O_3.

Such findings prompted us to initiate an investigation into the photochemistry of these impurities. A set of 47 reactions involving these impurities was simultaneously introduced, along with appropriate rate constants, into a computer routine for solving systems of chemical rate equations (developed by Robert Brown of the Center for Chemical Physics). In addition to reactions (1-3) detailed above, some of the other important reactions in the O_3 generator considered in this model were:

$$O(^1D) + H_2O = 2\ OH \quad (4)$$

$$O(^1D) + N_2O = 2\ NO \quad (5)$$

$$O(^1D) + CH_4 = CH_3 + OH \quad (6)$$

$$O(^1D) + O_3 = 2\ O_2 \quad (7)$$

$$O(^1D) + H_2 = OH + H \quad (8)$$

$$OH + O_3 = HO_2 + O_2 \quad (9)$$

$$OH + CH_4 = CH_3 + H_2O \quad (10)$$

$$OH + H_2 = H + H_2O \quad (11)$$

$$OH + CO = H + CO_2 \quad (12)$$

$$H + O_2 + M = HO_2 + M \quad (13)$$

$$CH_3 + O_2 + M = CH_3O_2 + M \qquad (14)$$

$$HO_2 + O_3 = OH + 2O_2 \qquad (15)$$

Chain Terminating Reactions

$$OH + OH = H_2O_2 \qquad (16)$$

$$OH + HO_2 = H_2O + O_2 \qquad (17)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (18)$$

The generation of the reactive radical, $O(^1D)$, via the photolysis of O_3 in reaction (3) is a critical step in this reaction sequence. Unfortunately, the rate constant for this reaction, k_3, is dependent on the radiation flux of the 1849 Å and 2537 Å mercury lines reaching the quartz photolysis tube, and is unique to every lamp and O_3 generator. Factors such as the separation between the lamp and the photolysis tube, the lamp temperature and voltage, the build-up of O_3 concentrations surrounding the lamp and the reflectivity of the O_3 generator housing will all affect the O_3 photolysis rate constant. In an effort to obtain an accurate value for this parameter, we measured the percentage loss of O_3, $(\Delta[O_3]/[O_3])\times 100$, as measured by a Dasibi UV photometer, by the addition of 775 ppm H_2O upstream of the O_3 generator. Water added downstream of the O_3 generator had no affect on the Dasibi readings, thus insuring that any observed changes were in fact due to photochemistry. The photolysis rate constant, k_3, was determined by fitting the observed O_3 loss, 4.3 percent, to the model in an iterative fashion. The resulting value of k_3, 0.125 s^{-1}, is within a factor of three of the value obtained by lamp flux estimates, 0.049 s^{-1}.

Additional experiments were performed in which the loss of O_3 was measured by the addition of other concentrations of H_2O vapor. These data are shown in figure 52 for two different initial O_3 concentrations — 1.27 ppm and 1.02 ppm. The computed profiles using the value of k_3 determined above are shown by the solid and dashed lines for the two different O_3 concentrations, respectively, and are in excellent agreement with the observed profiles. Such agreement strongly suggests that our model accurately describes the photochemistry occuring in our O_3 generator. Because of significantly larger uncertainties in the other experimentally determined O_3 losses, a refined determination of k_3 from a fit of all the data points was not justified.

In order to incorporate the previous results in a complete computer simulation of our GPT experiments, two additional computer runs were necessary. First, the concentrations of the various species at the output of the O_3 generator were put back into the computer model with all photolysis rates set to zero. This step represents the decay of the photolysis products during the transit time between the O_3 generator and the nitric oxide (NO) reaction chamber. Second, the concentrations generated in the previous step were put back into the model along with the addition of pertinent reactions involving NO. This step simulates the reaction sequence occurring during gas phase titration.

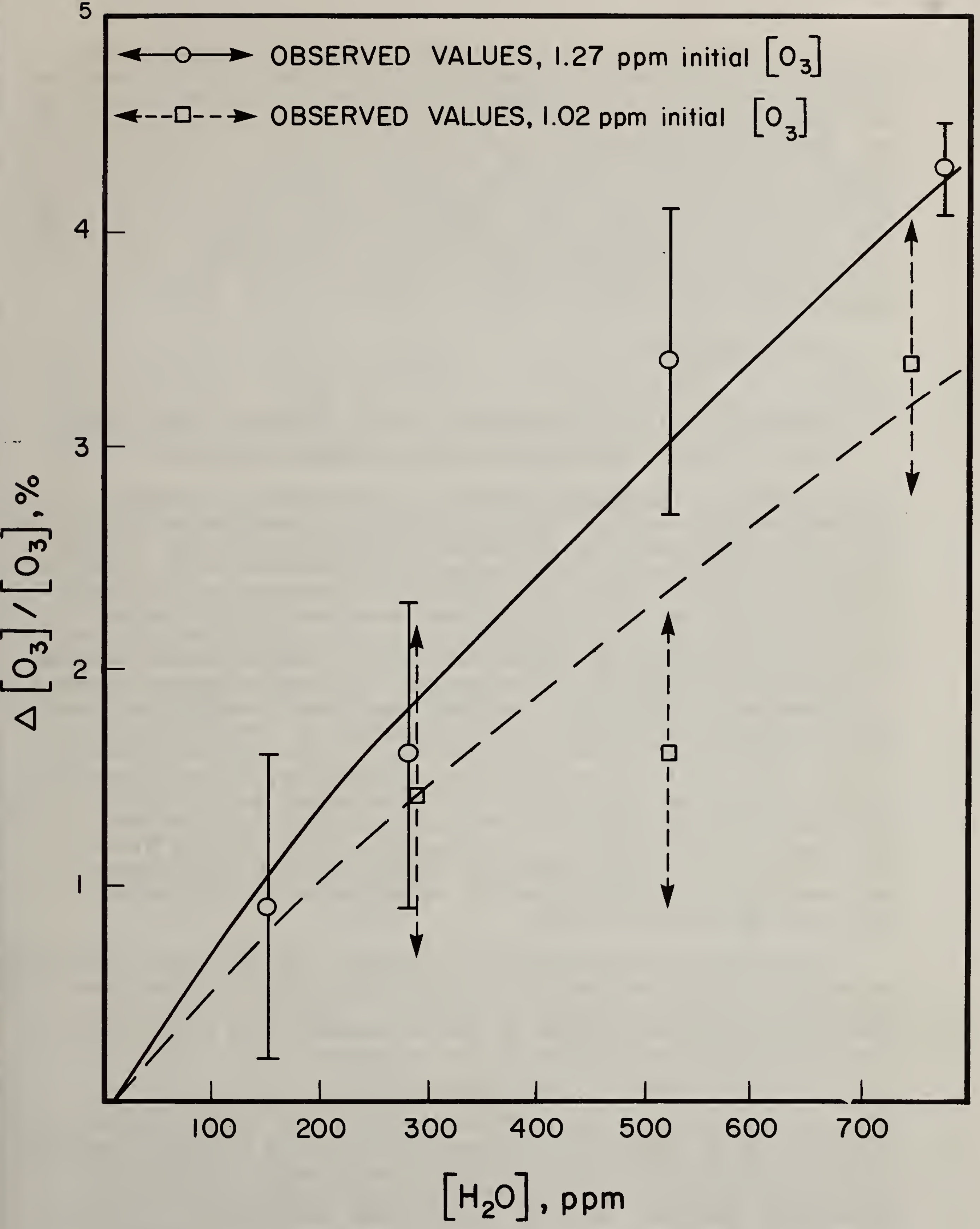

Figure 52. Predicted vs. observed O_3 losses for two initial O_3 concentrations. Points are the observed values, lines are predicted values.

While this analysis is not quite complete at this time, preliminary analysis using a limited set of reactions indicates that relative humidities as high as 50 percent would be required to generate a 2 percent increase in ΔNO relative to ΔO_3, as measured by UV photometry. The preliminary results also reveal a second important point, namely the existence of stable reaction products such as CH_3OOH, CH_2O, HNO_3, HNO_2, and H_2O_2 in the GPT sampling manifold. The presence of this last species is especially significant, since its existence has been speculated in GPT experiments employing KI determinations of O_3 in the presence of humidified air. In such cases, the generated H_2O_2 would be a positive interference in the O_3 determinations, and could possibly account for rather large positive biases found in previous KI determinations of O_3.

A. Fried, J. Hodgeson

11. Determination of Trace Gas Concentration by Infrared Tunable Diode Laser and Fourier Transform Infrared Spectroscopic Techniques

The demand for extremely sensitive analytical methods of measuring trace gas concentrations has resulted in the use of gas chromatography (GC) coupled with specific detectors, like the electron capture (ECD) and the flame photometric (FPD) detectors. These detectors are convenient and reliable at the high parts-per-million (ppm) level, however both detectors are generally unpredictable and non-linear at the ultra-trace levels (ppb, parts-per-billion, and ppt, parts-per-trillion). Alternative methods for measuring nitrous oxide (N_2O) and halocarbon F-11 (CCl_3F) at ambient levels have been surveyed, and two equally promising methods of infrared absorption spectroscopy have been investigated. One method uses a small tunable diode laser (TDL) as a source and provides resolution ($0.0004\ cm^{-1}$) many times greater than the Doppler width of an absorption line, low analysis time (milliseconds), and excellent reproduciability of sample analysis (±0.3 percent, relative standard deviation, RSD). The second method uses a Fourier Infrared Spectrometer (FT-IR) and provides wide coverage of the infrared spectrum with lower resolution ($0.06\ cm^{-1}$) of absorption lines, accurate frequency determination of absorption lines, and reproducibility of a few percent. Many more infrared absorbing gases can be measured within the same analysis with the FT-IR than with the TDL.

The greatest potential advantage of infrared techniques over conventional methods is that the spectroscopic technique allows both direct and comparative measurement of concentration in gas standards. Radiation at frequency ν passing through an absorbing gas at partial pressure, p in a sample cell of length, ℓ, is absorbed according to the Beer-Lambert Law,

$$I(\nu) = I_0 \exp \{-k(\nu)p\ell\},$$

where $k(\nu)$ is the absorption coefficient and I_0 is the baseline intensity. Therefore, one can determine gas concentration directly from prior knowledge of the absorption coefficient. Comparative measurements are possible by placing the gas sample in a cell and comparing its absorption to those generated by standards. Relative concentrations measurements at the ppm (by mole fraction) and the ppb levels have been made in this laboratory.

The determination of the absorption coefficient is crucial for the direct measurement of gas concentration by either the FI-IR or the TDL spectrometer. We have recently completed work on the measurement of the band strength by FT-IR of the major vibrational bands for halocarbon F-11 (CCl_3F). The strongest band, ν_4 (centered at 846 cm^{-1}), was investigated because it is situated in the "atmospheric window". Constituents of the earth's atmosphere do not absorb reradiated infrared radiation from the surface in this region of the electromagnetic spectrum whereas F-11 and other trace gases do absorb in this window and thus may be important to the radiation budget of the earth. Nine measurements were made of the integrated absorbance using the FT-IR for samples of F-11 at partial pressures between 64 and 400 pascals (0.4 and 400 torr respectively) in one and two cm long cells. A plot of the integrated absorbance (base 10, $\int A_{10} d\nu$) versus the pressure-pathlength product graphically displays agreement with Beer's law (figure 53). The slope of the line in figure 53 is equal to the band intensity, S, and this line yields $18.04 \pm 0.10\ cm^{-2}\ K\ Pa^{-1}$ ($1828 \pm 10\ cm^{-2}\ atm^{-1}$) for the ν_4-band. Therefore, gas concentrations can be calculated from knowledge of S, the integrated absorbance, and the length of the cell.

We have recently conducted a test of our diode laser absorption spectrometer system to determine the imprecision values for comparative measurements of samples from a set of gravimetric standards of nitrous oxide in air at the ppm level. The results of this test are shown in Table 35. The gravimetric concentration represents the value of N_2O in a cylinder based on gravimetry where the theoretical inaccuracy in weighing is less than 1 part in 10,000. The measured values refer to the average of several determinations based on the amount predicted from a linear function derived by a least squares fit of a calibration curve of the expected concentration versus the measured peak area. The relative difference, Δ percent, is the difference between the diode laser value and the gravimetric value divided by the gravimetric value, expressed in percent. The current imprecision for replicate samples is between ±0.1 and 0.3 percent (RSD).

Table 35. Diode Laser Measurement for PPM N_2O Standards.

Sample No.	Measured Concentration	Gravimetric Concentration	Δ%
1	241.4	241.3	+0.04
2	319.6	319.4	+0.05
3	337.0	337.5	-0.14
4	376.8	376.5	+0.07
5	488.4	488.4	0.00
6	523.6	524.8	-0.23
7	550.0	548.1	+0.34
8	591.9	592.6	-0.11

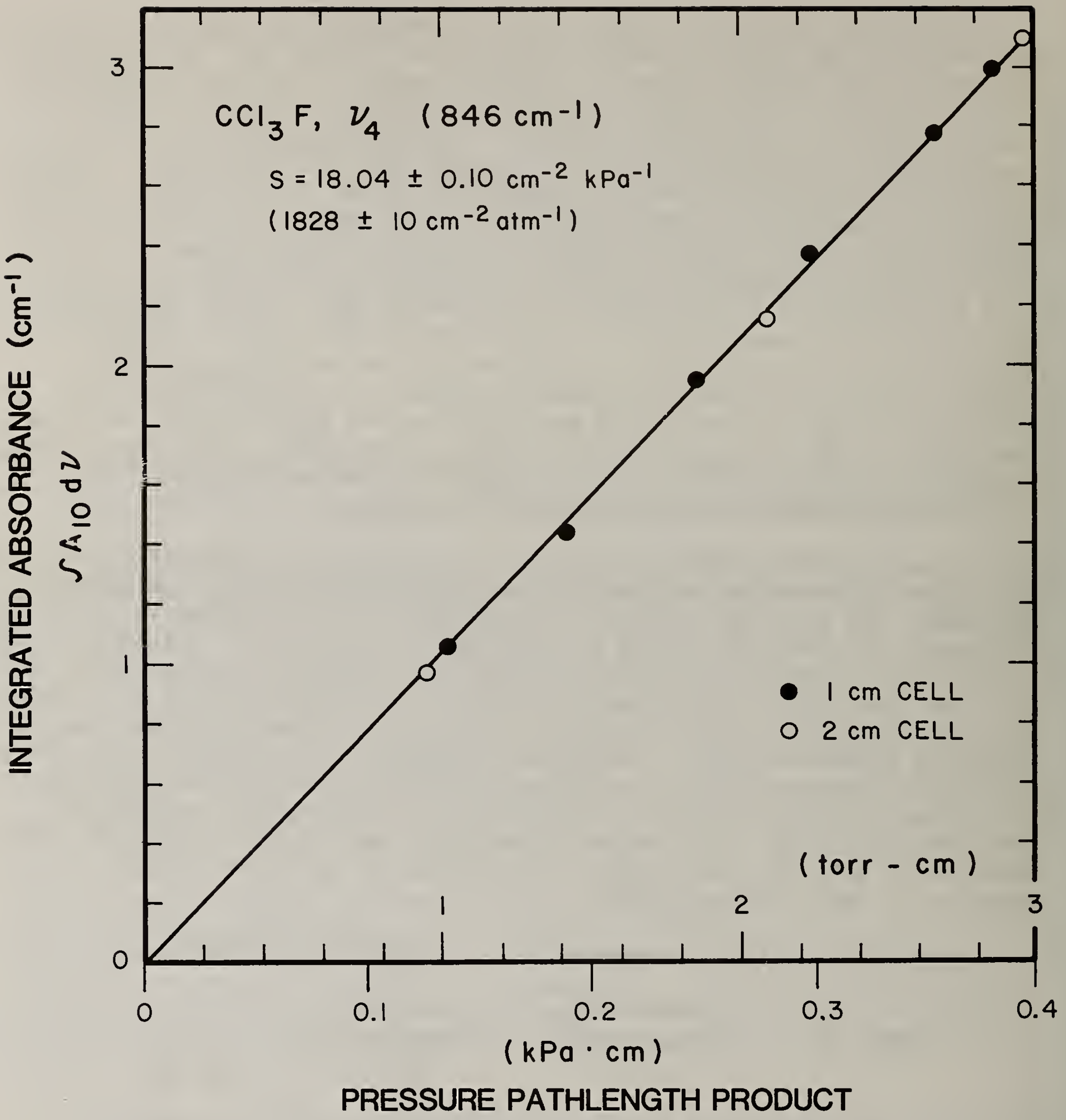

Figure 53. Band strength determination of ν_4 band of CCl_3F.

Our experimental goal is to measure concentrations of infrared absorbing gases at the ppb level with imprecisions of ±0.1 percent, the current limit of the best chromatographic results. The diode laser measurements in Table 35 were made in a 15.5 cm absorption cell at a pressure of 1.2 k pascals (9 torr). For N_2O, these measurements were not as accurate as those of electron capture — gas chromatography (EC-GC) at the ppm concentration level. However, we believe that if we use a 40 m total path white cell and if we can maintain the same signal to noise ratios as with the 15.5 cm long cell, then the diode laser may be useful for the determinations of ppb-levels of N_2O, comparable to those by EC-GC.

The FT-IR spectrometer will be used to complement the high resolution capability of the tunable diode laser. We plan to add a white cell to the present FT-IR spectrometer for trace measurement of infrared absorbing gases. The FT-IR system will allow identification of species and lines of interest. Once absorbing species are identified, the tunable diode laser spectrometer will permit discrimination from possible interfering lines and measurement of gas concentrations with inaccuracies of less than ±0.3 percent.

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12. Development of Ambient Nitrous Oxide and Halocarbon Standards

Concern has arisen during the past decade that possible increases of nitrous oxide (N_2O) and certain halocarbons may influence the equilibrium concentration of stratospheric ozone and consequently the radiative budget of the earth. Theoretical models which may be used to predict ozone concentration changes and radiative losses and/or gains require accurate measurement of the spatial and temporal concentrations of N_2O and certain halocarbons at low altitude to set boundary conditions for equations describing mass transport of these gases into the stratosphere. A number of recent laboratory intercomparisons have shown that variations in concentration values of greater than 10 percent were found for identical standards of ambient air with N_2O, halocarbon-11 (CCl_3F), and halocarbon-12 (CCl_2F_2) when analyzed by a number of different laboratories.

This report describes work in progress under a three year study jointly sponsored by the National Aeronautics and Space Administration (NASA) and NBS. The primary products of this investigation are the development of Standard Reference Materials (SRM's) of ambient N_2O (250-350 ppb), and halocarbons F-11 (50-250 ppt) and F-12 (100-400 ppt). The concentration ranges represent the lowest levels at which any gas standards will have been certified as SRM's. Preparation of nitrous oxide standards is nearing completion and work is progressing on the preparation of the halocarbon standards. An important milestone was accomplished in the verification of our nitrous oxide standards using two independent analytical methods.

A series of primary laboratory standards for N_2O have been prepared. These standards were used as the basis for a series of measurements made to answer questions concerning the current controversy on the value for the absolute concentration of N_2O in the earth's lower atmosphere. Our original intercomparison work [1], led us to conclude that a bimodal distribution existed in the assumed concentration of N_2O standards used by various laboratories which participated in the study. Indeed, the scientific literature currently contains values for atmospheric N_2O which may be divided into two distinct groups; one at approximately 300 and one at approximately 330 ppb.

In the present work, gas standards were prepared by a gravimetric technique and were measured to establish the absolute concentration of N_2O in the atmosphere. This measurement is important to our effort, because the value will determine the concentration range of the N_2O Standard Reference Materials (SRM's) which will be prepared and analyzed in the near future. In the gravimetric technique, the component and balance gases are weighed separately before and after addition to a cylinder. We prepare standards routinely by this method with accuracies of better than ±0.1 percent for dilution ratios of component gas to balance gas of 1:5000. Two dilution steps are required to prepare N_2O gas standards near atmospheric concentrations, first to ppm (parts-per-million), and then to ppb levels.

A set of "parent-standards" of parts-per-million of N_2O in air were prepared and subsequently analyzed by intercomparison with each other by gas chromatography (GC) using both electron-capture (EC) and ultrasonic (US) detectors. The parent-standard concentration values were chosen to be approximately the square root of the expected concentration value for atmospheric N_2O, so that identical pressures could be used in the two stages of dilution. The parent-standards were verified by comparing the amount predicted from a linear least squares fit of the expected concentration versus the measured peak area. The relationship indicated both by EC-GC and US-GC was essentially linear over the concentration range between 480 and 600 ppm, with typical values of the squared linear correlation coefficient (r^2) between 0.9995 and 1.0000. The relative difference between the gravimetric and the average measured concentration of each standard was less than ±0.1 percent.

The degree of linearity of the response versus the gravimetric concentration values from EC-GC and US-GC and the low uncertainty values for replicate samples of the parent standards were supporting evidence that the gas standards were prepared correctly. This evidence gave increased confidence for preparing subsequent standards in the following dilution step.

The second stage of dilution to ppb levels required the construction of a welded stainless-steel manifold with metal bellows valves for the transfer of the individual gases into the cylinder. The high sensitivity of the EC-GC allowed ultra-trace analysis of these standards. The gravimetric determinations were again verified by comparing the amount predicted from a linear least squares fit of the expected concentration versus the measured peak areas.

Samples of atmospheric air were collected by first evacuating a 2.3 liter electropolished stainless steel cannister fitted with a metal bellows vacuum valve to a pressure less than 0.13 Pascal (1 micrometer of Hg) in the laboratory, and then drawing the air sample by condensation into the cannister by opening the valve while the cannister was surrounded by liquid nitrogen. This procedure reduced contamination and provided an adequate sample for replicate analysis. The cannisters were analyzed by EC-GC after the water vapor had been eliminated by passing the sample through a P_2O_5 filter. The average concentration of N_2O in samples taken during the Spring of 1981 was found to be 299.8 ± 1.4 ppb (1s) for 21 samples measured. Therefore, the NBS certified standards for N_2O will be centered around 300 ppb.

Our N_2O standards at the ppb level were intercompared with three cylinders analyzed by R. F. Weiss at Scripp's Institution of Oceanography (SIO). Weiss measures atmospheric N_2O by comparing the ratio of the observed peaks in air due to CO_2 and N_2O using a modified US-GC procedure. The absolute value of CO_2 is based on both the measurement of the CO_2 concentration made by C. D. Keeling (SIO) and on standards made by Weiss with fixed

$N_2O:CO_2$ concentration ratios. The agreement between our method and SIO indicates no difference greater than ±0.2 percent (see Table 36).

Table 36. Intercomparison of N_2O Samples.
(ppb = parts-per-billion by mole fraction)

Sample	NBS Value	Value Determined at SIO
1	306.1 ± 1.0 ppb	305.8 ± 1.0 ppb
2	302.9	303.0
3	294.1	293.4

The preparation of gas standards of halocarbon F-11 ($CFCl_3$) presents problems somewhat different from those involved in the preparation of N_2O standards because F-11 exists as a liquid at room temperature. We have recently developed a microgravimetric technique for preparing standards of volatile liquids by weighing small quantities of the liquid contained in a capillary tube prior to its introduction into a gas cylinder. This method allows the preparation of low-ppm concentration standards in a step dilution with estimated inaccuracies of less than ±0.1 percent. Once the liquid is in the gas phase, subsequent dilution to ppt-levels is possible by a technique similar to that used for N_2O.

We propose to intercompare our gas chromatographic measurements with both diode and laser absorption and Fourier Transform Infrared measurements of N_2O, and halocarbons F-11 and F-12. These instruments will provide independent methods to verify the concentration of the various constituents in the gas standards.

Reference

[1] "Evaluation of Methodology for the Analysis of Halocarbons in the Upper Atmosphere", NBSIR-78-1480.

J. W. Elkins, E. E. Hughes

13. Standards for Measuring Toxic Organic Vapors in the Workplace Atmosphere

The major effort in the toxic organic standards project in FY81 was the preparation of primary gas cyclinder mixtures of a wide range of medium molecular weight organic solvents, the determination of the stability with time of these mixtures, the preparation and analysis of multi-component gas mixtures, and the certification of both gas mixtures in cylinders and permeation tubes containing benzene and perchloroethylene as Standard Reference Materials (SRM's). Major accomplishments were the development of a procedure to prepare gravimetric gas mixtures containing organic solvents with high vapor pressures, e.g., vinyl chloride monomer (VCM) and the completion of the long-term stability studies of benzene and perchloroethylene gas mixtures.

Gas mixtures containing high vapor pressure organic solvents in a matrix gas have been prepared gravimetrically using a modified capillary tube technique. Instead of filling the weighing tube with liquid organic by differential pressure, the tube is cooled with dry ice to create a temperature differential that draws the liquid into the tube. Gravimetric gas mixtures containing vinyl chloride monomer in a nitrogen matrix have been produced at concentration levels as low as 0.2 parts per million by mole (ppm) in a single step dilution. A set of mixtures prepared by this procedure in the concentration range of 0.5 to 10 ppm was compared with a set of mixtures prepared by the more laborious successive dilution method in the same concentration range. The results of this comparison showed that both sets yielded the same average FID response/concentration ratios but samples produced by the successive dilution technique showed greater imprecision.

Accurate multi-component gas standards for analytical techniques other than FID and electron capture (EC) have become more necessary as the quantitative ability of these techniques (e.g., GC/mass spectrometry) have been developed. Preliminary studies of gravimetrically-prepared mixtures of up to four organic solvents in a matrix gas demonstrated inaccuracies in predicted concentrations of less than 1 percent (relative) for each organic component at the one ppm concentration level.

Stability studies for several organic vapor/matrix gas mixtures in gas cylinders have been in progress for nearly two years. Periodically, all of the cyclinder standards are intercompared to detect any change in the relative response/concentration ratios of freshly-processed mixtures to mixtures that have been stored for longer time periods. If no difference in this ratio is noted between these mixtures, the concentrations of the cylinders are considered to be stable with time.

Benzene/air, benzene/nitrogen, and perchloroethylene/nitrogen mixtures have been studied for the past several years and no change in concentration has been observed. Vinyl chloride monomer, chloroform, toluene, and chlorobenzene, all in a nitrogen matrix have been observed for a one year period with no evident change in concentration.

Both gas cylinder mixtures and permeation tubes containing benzene and perchloroethylene prepared to our specifications have been obtained commercially and are in the process of certification for their issuance as SRM's. The results of the calibration of 17 benzene permeation tubes chosen randomly from a batch of 100 tubes in the certification process are shown in Table 37. The difference between the rates determined gravimetrically and the predicted rates based on their comparison with primary gas cylinder standards is less than ±1 percent (relative) in most cases. Since each tube in a batch will be individually calibrated, the uncertainty in the certified permeation rate of any SRM benzene permeation tube should be about ±1 percent (relative).

W. P. Schmidt

Table 37. Calibration of Benzene Permeation Tubes at 25.0 °C. Rates Determined by Gravimetry and by Comparison with Primary Gas Cylinder Standards.

Permeation Tube No.	Permeation Rate, 25.0 °C (Gravimetric)	FID[a] Response Dilution Flow = 100 cc/min.	Permeation Rate, 25.0 °C FID (vs. Grav. Stds.)	Δ Permeation Rate (FID – Grav.)
3	0.338 μg/min.	2504	0.343 μg/min.	1.5 % Rel.
5	0.369	2710	0.371	0.5
12	0.355	2600	0.356	0.3
13	0.355	2610	0.357	0.6
20	0.343	2512	0.344	0.2
22	0.372	2711	0.371	-0.2
26	0.358	2618	0.358	0.0
31	0.341	2492	0.341	0.0
53	0.341	2494	0.341	0.0
54	0.356	2595	0.355	-0.2
58	0.371	2713	0.372	0.2
66	0.377	2756	0.377	0.0
70	0.360	2638	0.361	0.3
76	0.339	2494	0.341	0.7
82	0.347	2527	0.346	-0.3
85	0.365	2658	0.364	-0.4
86	0.368	2696	0.369	0.3

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[a] Flame ionization detector.

14. Nitrogen Dioxide Standard for Stationary Source Emission Measurements

A series of four new SRM's consisting of nitrogen dioxide in air at concentrations of 250, 500, 1000, and 2500 parts per million (ppm) will soon be issued by NBS. The certification of these SRM's was particularly difficult because of the highly reactive nature of the NO_2 molecule and because of the absence of accurate analytical methods for NO_2. The reactivity of NO_2 precludes the use of gravimetrically prepared standards and the uncertainty of the reaction of NO_2 has thus far excluded the use of chemical or physical reaction for analysis on an absolute basis. Consequently, these mixtures were analyzed by conversion of the NO_2 to NO followed by analysis with instruments that respond only to NO and which have been calibrated with accurate NO standards. The results yielded a precise relationship between samples at the same concentration and a precise relationship between the various concentrate levels. The precise relationship between the various concentrate levels was further confirmed directly by UV photometric measurements of the NO_2.

Two major problems that had to be resolved before the program could successfully proceed were the determination of the efficiency of the conversion of NO_2 to NO and the difference in response of the NO_x analyzer to a nitrogen versus air balance gas. The solution to these problems and further confirmation of the accuracy resulting from the solution are described below.

The response of the chemiluminescent NO_x analyzer is dependent upon many things but the three that must be considered in this application are:

the NO content of the sample entering the cell, C_{NO};

the flow rate of the sample into cell, $f_{(s)}$;

and,

the quenching effect of the balance gas, Q.

When NO-in-N_2 standards are used to analyze NO_2-in-air samples, all three of these factors must be determined. The NO content of the NO-in-N_2 standard is known but when the NO_2-in-air is analyzed the amount of NO is dependent on the efficiency of conversion of the NO_2 to NO.

The converter efficiency was independently measured using an NO_2 optoacoustic detection system. The utility of this system has been demonstrated in the direct measurement of NO_2 in the intercomparison of NO, O_3, and NO_2 analytical techniques. The converter efficiency was determined by alternately directing the flow from a permeation tube calibration system through and around the catalytic converters into a stainless steel optoacoustic cell. The detection response obtained by flow through the converter, R_{conv}, and bypassing the converter, R_{bypass}, were used in the calculation of converter efficiency, CE, by the following relationship:

$$CE = \frac{(R_{bypass} - R_{bypass,\ baseline}) - (R_{conv} - R_{conv,\ baseline})}{(R_{bypass} - R_{bypass,\ baseline})} \qquad (1)$$

Using this procedure, a converter efficiency of 96.6 ± 0.6 percent was obtained over the NO_2 concentration range of 10 ppm to 120 ppm. Within the stated uncertainty, the converter efficiency did not show any NO_2 concentration dependence.

The effects of sample flow rate into the chemilumenescent cell and the background gas quenching were determined using the chemiluminescent nitric oxide analyzer and a high-rate NO_2 permeation tube system. The flow rate into the cell is regulated by a capillary tube and is dependent on the molecular weight of the gas (i.e., nitrogen versus air). The chemiluminescent quenching may also be dependent on the balance gas, again nitrogen versus air. Nitrogen and air were alternately used as balance gases through the NO_2 permeation tube system. The difference in the signals observed on the nitric oxide analyzer was a direct measure of the combination of these two effects since everything else was identical. The difference in the signals was determined to be 1.5 percent which is consistent with the difference in sample flows through the capillary.

Using air as a balance gas, the permeation tube system produced calibrant mixtures with sufficient flow to directly calibrate the NO_2 analyzer to analyze the NO_2/air mixtures at 250 and 500 ppm. The values determined by this method agree within 0.5 percent relative with the values calculated by using NO standards and applying the appropriate factors.

E. E. Hughes, W. D. Dorko, A. Fried

15. Intercomparison of Aitken and Cloud Condensation Nuclei Counters

An important measurement problem in the areas of cloud physics, air quality, and atmospheric modeling and characterization is that of detecting and quantitating the concentration of Aitken and Cloud Condensation Nuclei (CCN). (Aitken nuclei are those particles capable of being activated as condensation nuclei at supersaturations of the order of 200 percent, whereas CCN are particles or aerosols capable of being activated as condensation nuclei under atmospherically realistic supersaturations of between 0 percent and 1-2 percent.) A variety of Aitken counters and CCN counters have been developed but their performance has never been rigorously intercompared nor has a "standard" counter been agreed upon as a reference for calibration or comparison. During the past year we have intercompared two Aitken counters — a Pollak counter and a Thermal Systems Incorporated (TSI) Condensation Nucleus Counter (CNC) — and have also, as participants in the 1980 International CCN Workshop, intercompared these instruments with CCN counters of other participants.

The Pollak counter, which has been in wide use for over 20 years, measures Aitken nuclei concentrations by overpressuring an air sample during which time it is saturated with water vapor, and then quickly expanding the volume to achieve supersaturation and subsequent nuclei activation and growth by condensation of the vapor. The concentration of droplets formed is measured by determining the decrease in transmittance of a light beam through the sample. The transmittance must be calibrated against concentration of the aerosol.

The TSI CNC is a continuous flow instrument and works on a completely different principle. The sample stream is first saturated with alcohol vapor (n-butyl alcohol) and then passed through a chilled condenser tube (kept at 25 °C below the saturator) where supersaturation occurs, the nuclei are activated, and the resulting droplets grow to 5 to 10 μm in diameter. The sample containing droplets then passes into a viewing/detection region. For sample concentrations below 1000 cm^{-3}, the droplets are counted individually by detecting the pulses of scattered light resulting when a droplet passes through a light beam in the detection region. The instrument operates in an absolute or self-calibrating mode in this case and one needs know only the flow rate and the count rate to determine the concentration. (At higher count rates it is necessary to apply a correction for coincidence losses, but this is easily accomplished.) At concentrations above 1000 cm^{-3}, the TSI CNC operates in a photometric mode in which the photodetector circuit measures the intensity of light scattered from all the droplets present in the detection volume. The photodetector output then must be calibrated as a function of concentration of the aerosol, and the resulting calibration incorporated into the electronics of the instrument. In addition to flow rate, parameters such as residence time in the condenser tube, vapor and heat diffusivity, photodetector linearity, and optics cleanliness all affect the calibration of the instrument.

We have found, in a comparison of the Pollak and TSI CNCs, that the instruments are in agreement to within 10 percent when the TSI is in the single or absolute count mode (see figure 54). (This result confirms an earlier study [1] which indicated that the Pollak calibration curve tends to underestimate the concentration by some 10 to 20 percent at low values (below 1000 cm^{-3}) when compared to an "absolute" Aitken counter which used photographic detection of the droplets and subsequent visual counting.) The upper curve of figure 54 calls attention to several precautions that must be taken in using the TSI in the photometric measurement mode. The non-linear portion of the log-log plot of the TSI-vs-Pollak results was due to dirty optics in the instrument. Light scattered from dirt or a film on the optics contributes a small background signal that is integrated into the signal resulting from light scattered by the droplets. The relative contribution of this background decreases as concentration increases and, in this case, becomes negligible above 2000 cm^{-3}. The linear portion of the upper curve is parallel to an extrapolation of the lower curve (absolute counting mode) which suggested a miscalibration was likely. A check of one calibration parameter (the photodetector pulse height) showed that the instrument was indeed out of calibration. This was due at least partly to the fact that we were operating the instrument at an appreciably higher altitude (Reno, Nevada, 1371 M) than that at which it was calibrated (St. Paul, Minnesota, 266 M). There is no direct way to adjust the calibration and our conclusion is that one must exercise great caution in using the instrument in the photometric mode for absolute concentration determinations. We also note, however, that it still provides reliable relative measurements in this concentration range and has the advantage of providing a continuous, real-time measurement.

We have also compared the performance of the Pollak and the TSI CNCs with that of cloud condensation nucleus counters. Under most conditions the CCN counters will give lower values because they detect and measure only those nuclei which are activated at a few percent supersaturation. However, when the test aerosol is a monodisperse, submicrometer aerosol, it will all be activated by these devices and the two different types of instruments should give the same results. Our results of an intercomparison of a representative CCN counter (the University of Missouri at Rolla continuous-flow diffusion chamber) with the Pollak and the TSI indicated that this particular instrument read about 20 percent and 10 percent higher than the Pollak and TSI counters, respectively. This is considered quite good agreement.

The results of the intercomparison have served to validate a large body of data that has been taken with the Pollak over the last twenty-some years. The study also identifies the conditions under which the TSI CNC can be used as a self-calibrated, absolute counter and the conditions under which one must exercise caution (i.e., the photometric mode) in interpreting the accuracy

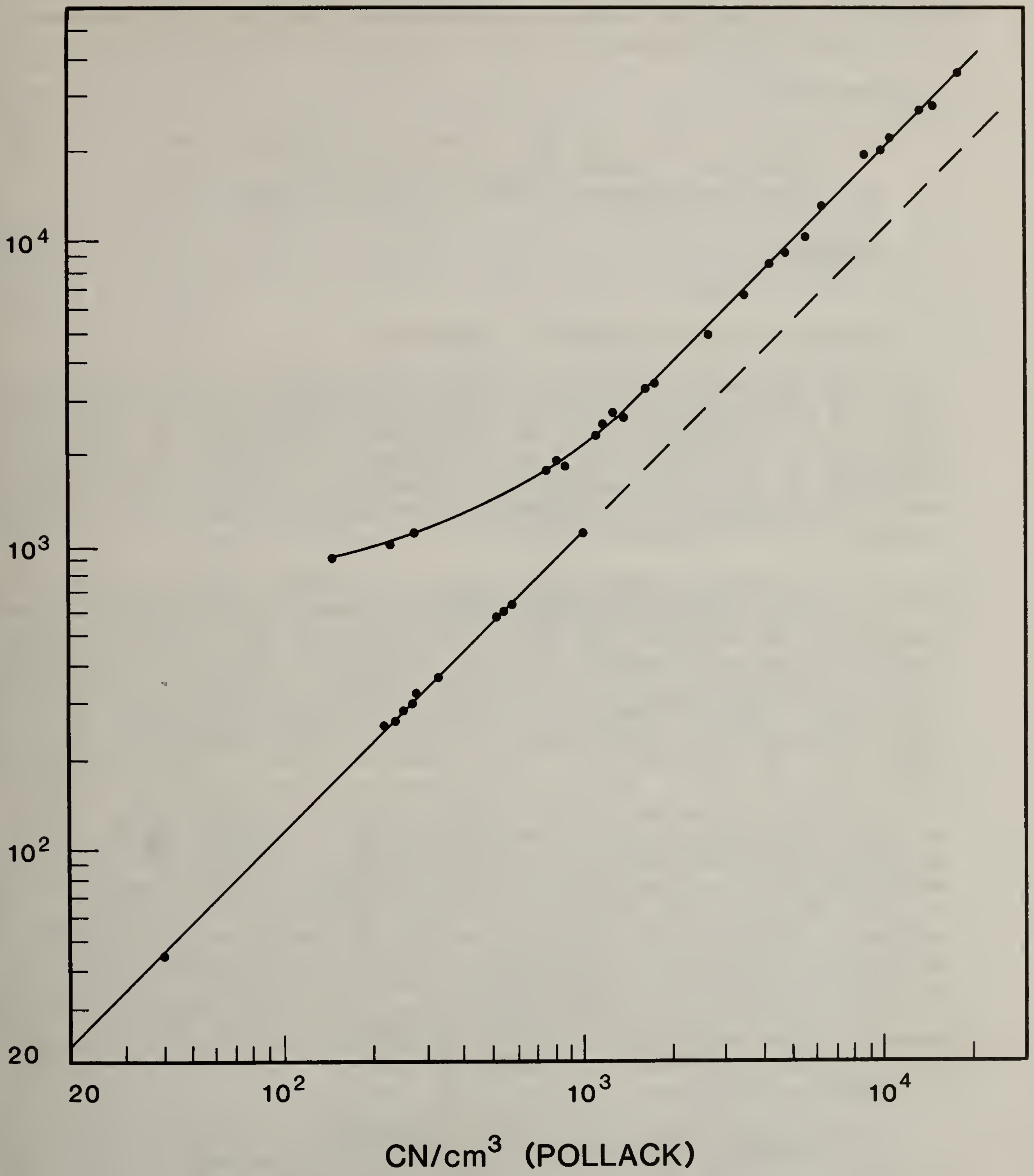

Figure 54. Intercomparison of TSI and Pollack Condensation Nuclei concentration measurements (CN/cm^3). The TSI counter was operating in the single count mode in the lower curve and in the photometric mode in the upper curve.

of the results. On the basis of our results, we recommend that the TSI be used in the single-count mode exclusively and we plan to evaluate the feasibility of developing an automated dilution system that will allow one to always present the instrument with sample concentrations below 1000 cm^{-3}.

Reference

[1] Emmanuel, M. B.; Squires, P. Absolute calibration of a photoelectric condensation nucleus counter at low values of nucleus concentration, PAGEOPH, 72:268-283 (1969.

R. L. McKenzie

16. Nuclear Environmental Analytical Chemistry

During the past few years our research in this area has been directed toward the development of radiocarbon dating techniques for the identification of sources of carbonaceous gases and particles in the atmosphere. These efforts remain our primary focus, but the scope of the program has expanded somewhat to encompass the combined use of nuclear, (stable) isotopic and chemical data together with environmental models to increase our basic understanding of the environmental system.

A. Environmental radiocarbon results. A continued effort has been made this past year to apply radiocarbon (^{14}C) measurements to atmospheric carbonaceous particles and gases for source identification. The basic model for use of ^{14}C as an environmental tracer is isotopic dilution; that is, radiocarbon is present in all living ("biogenic") matter, and, since it decays with a half-life of 5730 years, it is essentially absent from fossil fuel. The relative proportions of biogenic and fossil source components is thus deduced from the observed $^{14}C/^{12}C$ ratio compared to that in the biosphere ($^{14}C/^{12}C \approx 1.5 \times 10^{-12}$). Because the two-source assumption (fossil, biogenic) is quite good, and because isotopic composition is quite robust with respect to changes due to reaction or transport, the $^{14}C/^{12}C$ ratio is intrinsically reliable for (carbonaceous) source apportionment. For most studies involving measurement of ^{14}C on particulate samples containing milligrams carbon our low-level counting (llc) facility utilizing miniature gas proportional counters is ideal, but for individual species the tandom Accelerator Mass Spectrometer (AMS) approach of counting single ^{14}C atoms on microgram quantities is necessary. Activities this year have included ^{14}C measurements by llc on particulate samples collected in Houston, Texas and Elverum, Norway for urban source identification, Shenandoah Mountains for local natural pollution affects, and Pt. Barrow, Alaska for long range transport of elemental carbon.

B. Low-level counting measurement techniques. Our work on extending the state-of-the-art of small sample decay counting [low level counting (llc)], minature proportional counters), and direct atom counting [accelerator mass spectroscopy (AMS)] (tandem accelerator) has continued. One emphasis has been the further investigation of sample preparation techniques for AMS and improved sample prepararion, radiocarbon (β^-) measurement and data reduction-quality control methods for llc. We have instituted an improved means of quality control involving "segmented counting" with the automatic output of six control charts for each measurement. In this process, each major counting period (typically 8-24 hours) is subdivided into approximately 10 counting intervals, and important parameters — such as barometric pressure, guard count rate, meson rate, anticoincidence rate, etc. — are separately monitored. Occasional localized problems (as from a passing thunderstorm) can be quickly deduced from the multiparameter control chart.

C. Sample preparation research. For each carbonaceous sample type being investigated, chemical methodology for quantitative conversion of sample to carbon dioxide is extremely important. To analyze atmospheric CH_4 samples, (18 samples were collected at NBS), a means of converting CH_4 to CO_2 was developed which uses a catalyst (Hopcalite) at ~400 °C in the presence of oxygen.

In addition, each particulate sample is unique to the collection site, and contains varying nitrogen and sulfur compounds that upon combustion are transformed into impurities which affect llc counting efficiencies. It has therefore been necessary to refine our purification procedure for nitrogen and sulfur oxides and we are currently developing purification techniques to remove Rn-222 from CO_2 samples. Rn-222 may be either inherent in sample or occur as a result of combustion. We have found gas chromatographic techniques to be most useful here.

If sample sizes are in the microgram range, an AMS approach to ^{14}C assay will be required. For this reason some research has been devoted to the combustion of microgram quantities of carbonaceous samples to carbon dioxide and subsequent chemical conversion to carbon (amorphous form) to be used as a solid source for AMS. The technique utilizes a closed vycor break-seal tube for quantitative combustion to CO_2 and subsequent transfer of CO_2 to a second vycor break-seal tube for reduction to carbon in the presence of Mg metal.

D. Radiocarbon and receptor modeling. The information content from radiocarbon measurements can be enormously enhanced by combining it with "serial" or "parallel" chemical or physical information. By serial information, we refer to ^{14}C data which results from a serial selection process according to time, location, particle size, or chemical species. Parallel information refers to multidimensional data, that is data arising from the simultaneous evaluation of a single sample according to such characteristics as isotopic composition (^{13}C, ^{14}C), inorganic composition, organic composition, and morphology. In a sense serial data, collected for a series of samples, provides the necessary input for multivariate analysis (including time series and principal component analysis); parallel data from a single sample yields the input for least squares analysis (chemical mass balance). Such a combination of ^{14}C measurements, which yield a robust indication of the biogenic fraction, with complementary physicochemical data is clearly a most powerful approach for receptor model validation and precise estimation of *individual* carbonaceous source components. (Radiocarbon alone, of course, will not resolve individual biogenic or individual fossil carbon sources.)

An initial step taken towards the modeling problem has been incorporation of a multi-facet routine called "Arthur" for pattern recognition on large data sets and the addition of multi-dimensional scaling routines and parametric mapping.

L. A. Currie, R. W. Gerlach, G. A. Klouda, G. B. Tompkins

17. Development and Evaluation of Personal Particulate Dosimeters

The development and testing of the NBS portable particle sampler has been completed. Much of this work involved the use of the wind tunnel which was built and tested last year. Several prototype samplers were made and have been sent to the project sponsors, the Environmental Protection Agency, and to Dr. John Spengler of the Harvard Medical School, Boston for evaluation. The NBS sampler differs from existing portable samplers in that it collects both the inhalable (5-15 µm) and respirable (<3 µm) size fractions and has a higher flow rate for longer sampling periods. Besides developing the NBS sampler, we have tested the particle size collection characteristics of the 10 mm nylon cyclone used in the Harvard Medical School sampler and the H & H (of Toronto) aluminum cyclone.

NBS Sampler

The NBS sampler consists of three particle collection elements — an inlet, a coarse filter, and a fine filter — in which each element collects successively smaller sized particles.

The inlet was designed by Drs. Walter John and Steve Wall of the University of California, Berkley and was rescaled by us to adapt to the NBS sampler. The inlet is cylindrically symmetrical to minimize the effects of wind direction. It removes the very large particles from the sample by impaction and passes the smaller particles on to the filters. A cross section of the inlet is shown in figure 55. Representative data showing the collection efficiency vs. wind velocity with the 15 µm conical insert in place is shown in figure 56. Here, the diameters range from 4 to 7 µm. The collector efficiency for particles below 7 µm decrease slightly with wind speed.

We tested the coarse filter collection efficiency in more detail than reported last year, since this element of the sampler separates the respirable size fraction from the larger or inhalable size fraction. Figure 57 shows the filter collection efficiency and Table 37 gives the corresponding 50 percent cut point characteristics. The effects of particle bounce, particle density, and filter loading are of particular interest. For total filter loadings under 400 µg the cut characteristics did not change, as shown in figure 57. The coarse filter suffers some particle bounce, and liquid particles, which do not bounce, are collected more efficiently than solid ones. However, liquid particles are atypical for ambient aerosols in this size range. Particle density affects the cut characteristics only slightly.

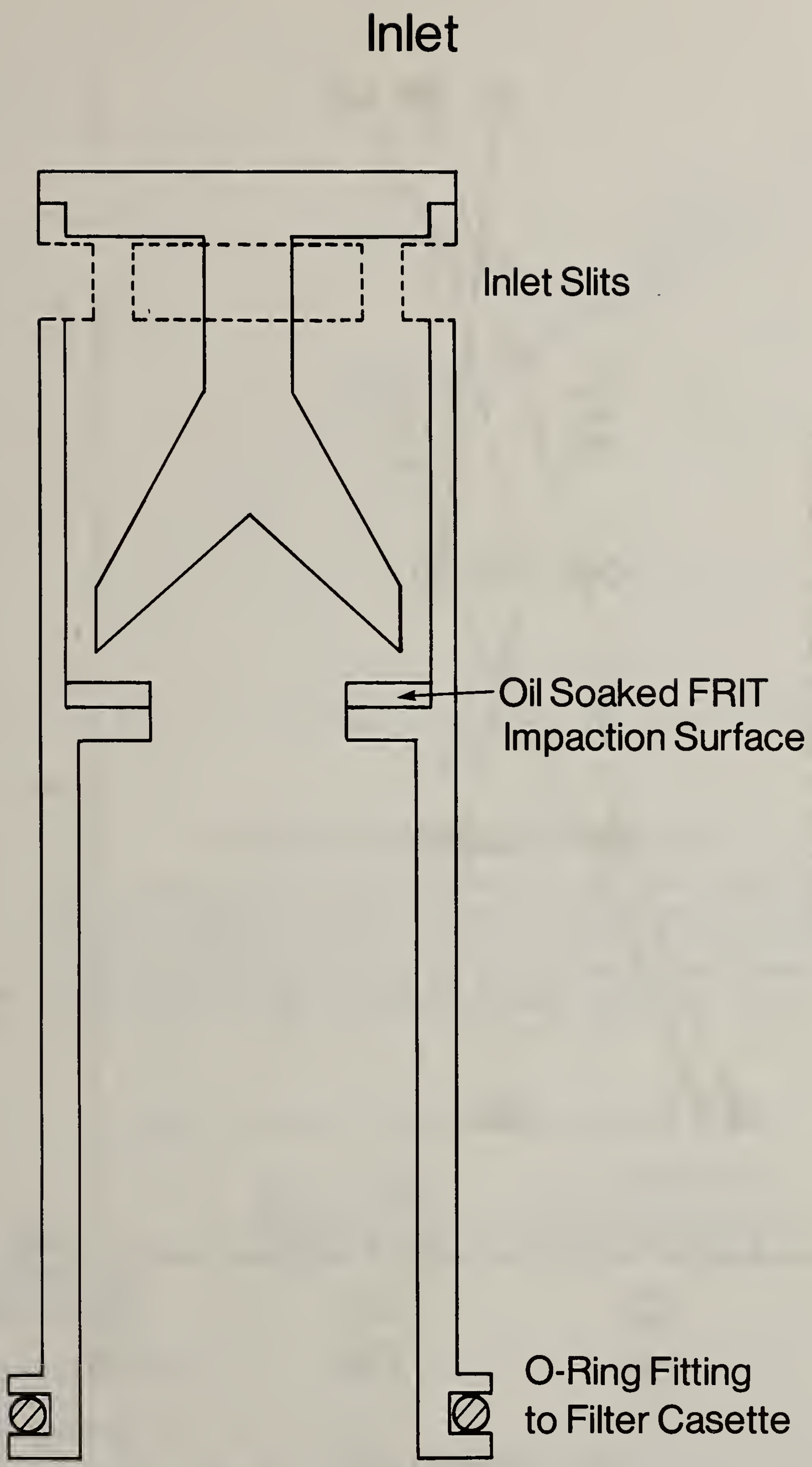

Figure 55. Scale drawing of the NBS Sampler inlet.

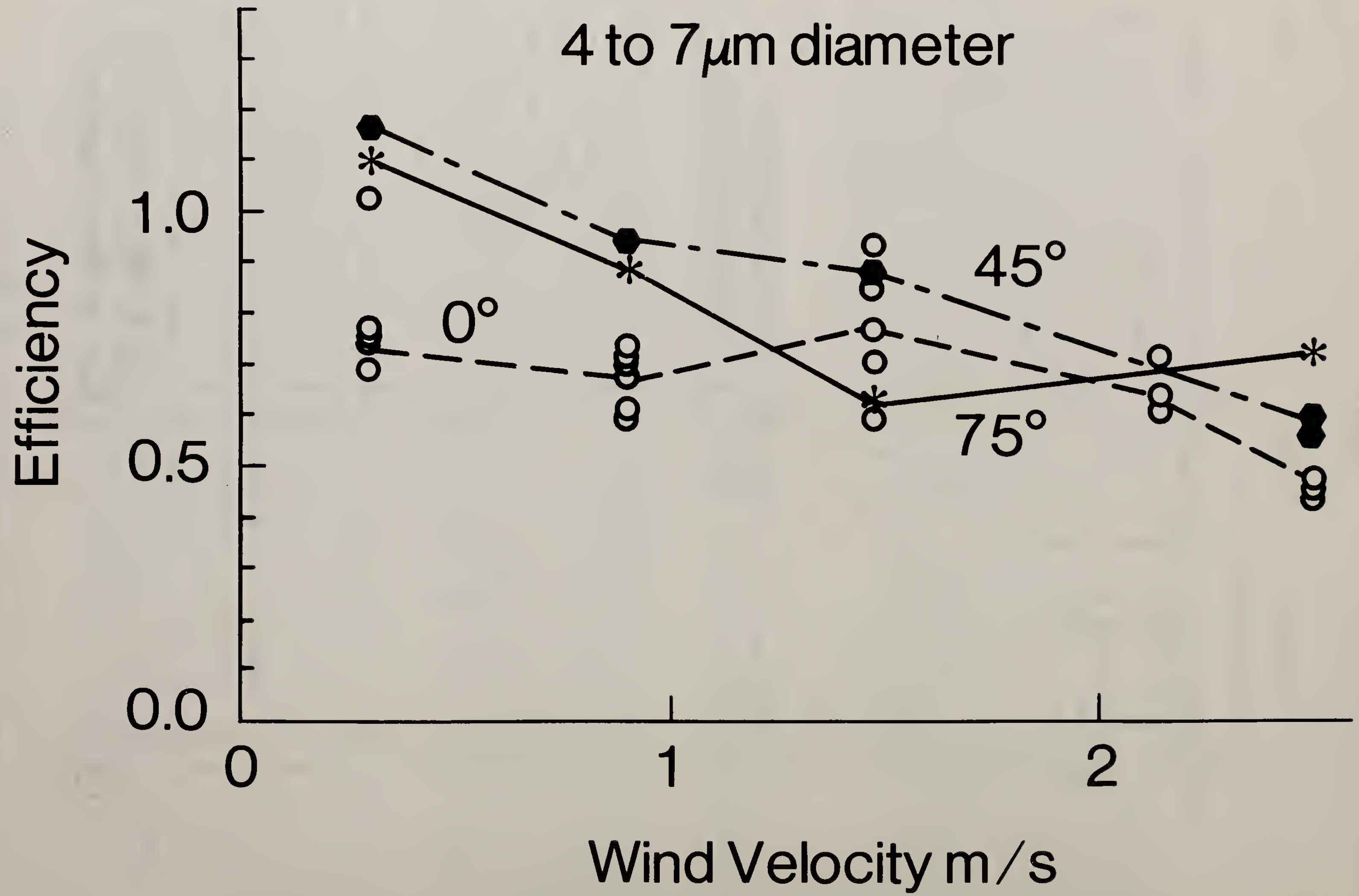

Figure 56. Collection efficiency of the inlet as a function of wind speed for 4 to 7 μm diameter particles at 0, 45, and 75 degrees relative to the wind direction.

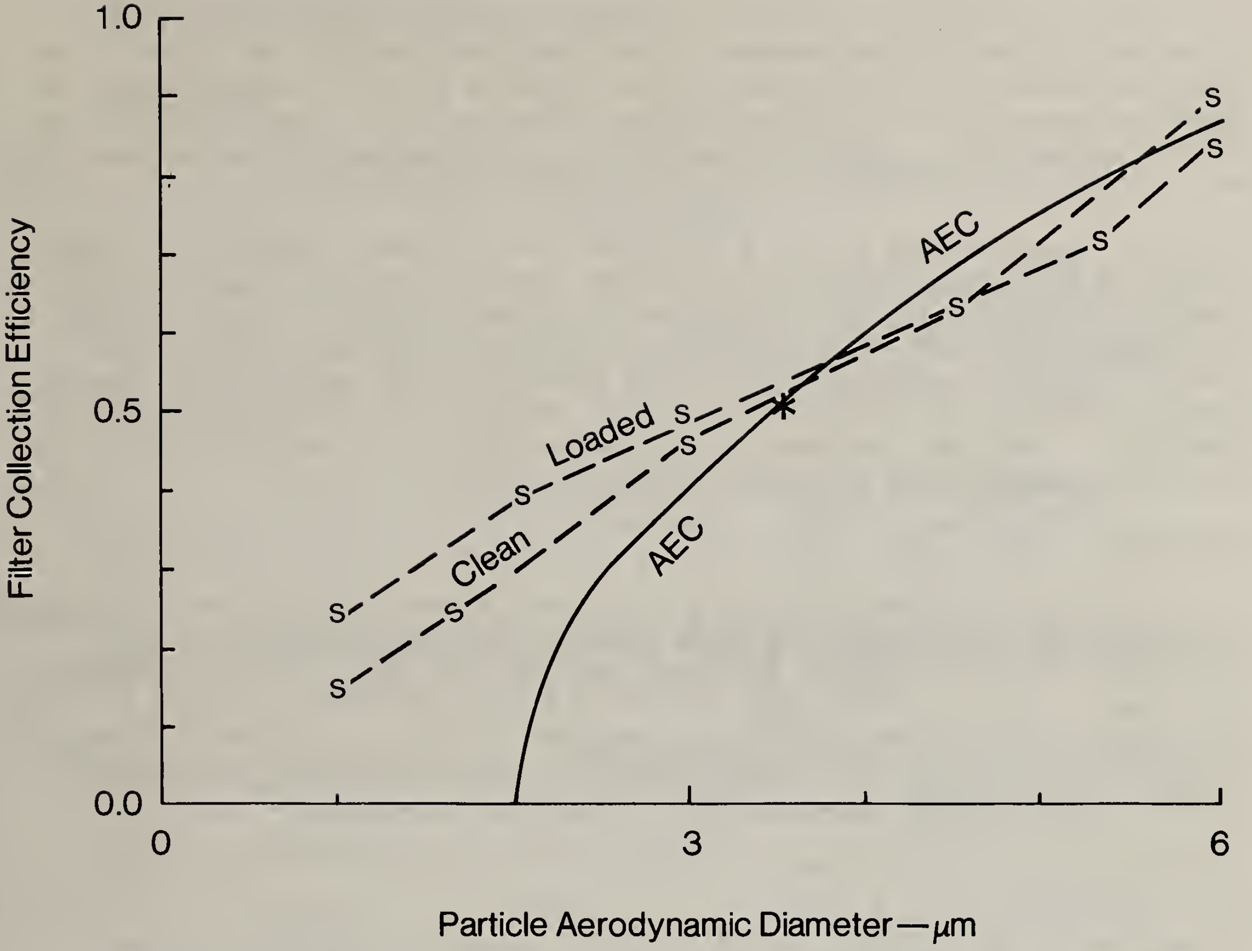

Figure 57. The filter collection efficiency is the mass fraction of particles reaching the filter that stick on the filter. The efficiencies of the filter before (Clean) and after collecting (Loaded) a 150 to 400 μg sample are shown along with the AEC recommended respirable cut curve.

Table 37. Cut Point Characteristics.

Device	50% Cut Point Diameter - μm	σ_g = Geometric Standard Deviation
AEC respirable recommendation	3.4	2.7
NBS coarse filter	3.2	2.8
10 mm cyclone	2.6	1.7
H & H cyclone	5.7	1.9

The fine filter is intended to catch all of the remaining particles. Since this filter is the sampler element that requires the most work of the pump, we selected a Teflon fiber filter, gaining a three-fold reduction in pump work over that of similar filters at the cost of a 1 to 2 percent loss of 0.1 μm particles. Loadings heavier than anticipated with normal use did not plug the fine filter or change the sampler flow rate.

The sampler draws air at 6 L/min for over 24 hours, sampling a larger volume of air than other similar devices. This is important because for ambient air, obtaining sufficient sample for weighing is often a problem. The sampler, enclosed in a case lined with foam, operates quitely. The interior of the case serves as a pulse damper so that the air flow through the size discriminating elements is much smoother than in other similar samplers. Tools are not required to change filters or sampler parts. All parts are commercially available except the inlet.

Cyclones

The cut or cyclone efficiency curves which show the fraction of particles caught by the cyclones vs. particle diameter were determined for both cyclones. We characterized the 10 mm cyclone with the 1.7 L/min pulsation air flow of the Harvard sampler and the H & H cyclone with a steady 1.7 L/min air flow. The cut characteristics are given in Table 37, along with the characteristics for the AEC recommended respirable cut point and the NBS sampler coarse filter cut.

D. S. Bright, R. A. Fletcher

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Newbury, D. E., "A Monte Carlo Electron Trajectory Simulation for Analytical Electron Microscopy," 3rd International Workshop on Analytical Electron Microscopy, Vail, CO. (7/13-16/81).

Newbury, D. E., "Application of Microprobe and Surface Analysis Techniques to Technological and Biological Problems," Labcon 81, Chicago, ILL., (9/15/81).

Newbury, D. E., "Observations on the Mechanisms of High Resistance Junction Formation in Aluminum Wire Connections," American Society for Metals Local Society, Albuquerque, NM (9/23/81).

Newbury, D. E., "Recent Developments in Microbeam Analysis Techniques," Northern California MAS Local Group, San Francisco, CA (4/29/81).

Newbury, D. E., "Backscattered Electron Detectors for Scanning Electron Microscopy," Metropolitan MAS Local Group, Brunswick, NJ (5/21/81).

Newbury, D. E., "Recent Developments in Microbeam Analysis Techniques," Southwest MAS Local Group, Albuquerque, NM (9/24/81).

Pella, P. A., "XRF Analysis of NBS Ternary Alloys and Fused Samples Using Empirical and Fundamental Parameter Data Reduction Techniques," 7th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, PA (10/1/80).

Small, J. A., "Error in Asbestos Analysis: Operator Error and Filter Homogeneity", Scanning Electron Microscopy, Dallas, TX (4/81).

Small, J. A., "Errors Observed in the Analysis of Particle Mixtures by Overscanning," Scanning Electron Microscopy, Dallas, TX (4/81).

Small, J. A., "Quantitative Particle Analysis in Electron Beam Instruments," SEM, Dallas, TX (4/81).

Small, J. A., "Analysis of NBS SRM #1648 For Use as a Matrix Material in the Development of Asbestos Filter Standards," NBS/EPA Workshop on Asbestos Standards, Washington, D.C. (10/80).

Simons, D. S., "The Study of Crystallographic Contrast in Ion Microprobe Analysis of Incone," 3rd International Secondary Ion Mass Spectrometry Symposium, Budapest, Hungary (8/31/81).

Steel, E., "Minimization of Operator Error in Analytical Electron Microscopic Analysis of Asbestos Samples," Asbestos Standards Workshop, Washington, D.C. (10/80).

Steel, E., "Preparation of Thin Film Glass Standards for Analytical Electron Microscopy," Microbeam Analysis Society Annual Meeting, (7/81).

3. Committee Assignments

Harry Rook
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 Atmospheric Analysis
Member, ASTM D-22.03 Monitoring Instrumentation
Member, ASTM E-29 Particle Size Measurement
Member, ASTM E-29.04 Characterization of Liquid Particles

Arnold Bass
Member, ASTM D-22.02 Methods of Sampling and Analysis
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

Lloyd Currie
- Member, Intersociety Committee - Methods of Air Sampling and Analysis
- Member, Analytical Letters - Editorial Board
- Member, International Committee for the Calibration of the Radiocarbon Time Scale
- Member, Model Validation Subcommittee - Receptor Modeling Workshop
- Member, CAC Computer Utilization Committee
- Member, Organizing Committee - 1981 International Conference on Residential Solid Fuels

William Dorko
- Member, American Chemical Society, Washington Section, Board of Managers

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

Jimmie Hodgeson
- Member, ASTM D-22 Atmospheric Analysis
- Member, ASTM D-22.02 Manual Methods
- Member, ASTM D-22.03 Instrumental Methods
- Member, ISO/TC 146/SC3 Air Quality/Ambient 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
- Member, Microbeam Analysis Society (National Council)
- Member, ASTM E-2 Emission Spectroscopy
- Member, ASTM E-2.04 Standard Reference Materials

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

4. Other

a. Seminars

October 16, 1981 - Dr. William Fairbanks, Colorado State University, Measurement of Low Iodine 129 Isotopic Concentration by Laser Fluorescence" (NBS sponsor: H. Rook)

November 14, 1980 - Dr. Bernhard Lehman, Oak Ridge National Laboratory, "Counting Noble Gas Atoms with Lasers--a New Approach to ^{39}Ar and ^{81}Kr Dating" (NBS sponsor: L. Currie)

January 28, 1981* - Dr. Hal Rosen, University of California, Joint Colloquium with OEM "Soot in the Arctic" (NBS sponsor: L. Currie)

February 10, 1981* - Prof. Jane Fox, University of Illinois Joint Colloquium with Chemical Kinetics Division, "A Chemical Instability in the Stratosphere" (NBS sponsor: J. Elkins)

February 25, 1981 - Dr. R. D. Leapman, National Institutes of Health, "Materials Characterization Using Electron Energy Loss Spectroscopy" (NBS sponsor: Dale Newbury)

March 25, 1981* - Dr. Louis Codispoti, Bigelow Laboratory for Ocean Science, Joint Colloquium with Office of Standard Reference Materials," Temporal Changes in Carbon Dioxide (pCO_2) in the Surface Waters of the Bering Sea" (NBS sponsor J. Elkins)

April 1, 1981* - Mr. Joseph Krasnec, Univeristy of Idaho, Joint Colloquium with Office of Environmental Measurements, "Spatial and Temporal Distribution of Methyl Chloroform in the Earth's Atmosphere" (NBS sponsor: J. Elkins)

April 22, 1981* - Dr. Walter W. Berg, National Center for Atmospheric Research, Joint Colloquium with Office of Environmental Measurements, "A New Look at the Chlorine-Bromine Synergism" (NBS sponsor: A. Fried)

May 20, 1981* - Dr. Michael J. Kurylo, NBS Joint Colloquium with Chemical Kinetics Division, "HO_x Reactions of Stratospheric Importance". (NBS sponsor: D. Newbury)

May 26, 1981 - Dr. R. G. Downing, Texas A&M University, "Isotopic and Elemental Heterogeneitics of the Noble Gases in the Solar System" (NBS sponsor: D. Newbury)

May 27, 1981 - Prof. Nai-Teng Yu, Georgia Institute of Technology, "Raman Spectroscopy with Intensified VIDICON & RETICON Detectors" (NBS sponsor: E. Etz)

June 22, 1981* - Dr. Lado Kosta, Institute Jozef Stefan, Yugoslavia Joint Colloquium with Office of Standard Reference Materials "Reference Analytical Methods for Trace Analysis of Standard Materials" (NBS sponsor: H. Rook)

June 24, 1981 - Professor Edward S. Macias, Washington University, "Urban Haze: The Importance of Carbonaceous Particles". (NBS sponsor: R. Fletcher)

July 9, 1981 - Dr. John Titchmarsh, AERE Harwell, England "Use of Particle Analysis of STEM in Studies of (1) Reveisible Temper Embrittlement and (2) Irradiation Induced." (NBS sponsor: D. Newbury)

July 27, 1981 - Dr. Arnold P. Von Rosenstiel, Applied Research Organization (TNO), Apeldoorn, The Netherlands, "Analysis of Fly Ash by High Voltage Electron Microscopy and Secondary Ion for Mass Spectrometry." (NBS sponsor: J. Small)

*Denotes Jointly Sponsored Colloquia

b. Workshops

"Workshop on Certified Reference Materials" held at NBS May 28, 1981 (E. E. Hughes).

"3rd International Workshop on Analytical Electron Microscopy," July 13-16, 1981. Vail, Colorado (D. E. Newbury session organizer and chairman).

Asbestos Standard Workshop. NBS 10/80. (J. A. Small, organizer and chairman).

"Willard F. Libby Memorial Symposium on Nuclear and Radiochemistry," New York, NY (August 25, 1981. L. A. Currie, organizer and chairman).

c. Standard Reference Materials

X-Ray Fluorescence

1620a, 1621b, 1622b Sulfur in Residue Fuel Oil

Austenite in Ferrite
1226 Alloy
1155, 1155A Alloy
1173 Alloy
1270, 1270A 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

1661 SO_2/N_2 500 ppm
1664 SO_2/N_2 2500 ppm

1665 C_3H_8/Air 3 ppm
1666 C_3H_8/Air 10 ppm
1667 C_3H_8/Air 50 ppm
1668 C_3H_8/Air 100 ppm
1669 C_3H_8/Air 500 ppm

1674 CO_2/N_2 7%
1675 CO_2/N_2 14%

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

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

2619 CO_2/N_2 0.5%
2620 CO_2/N_2 1%
2621 CO_2/N_2 1.5%
2622 CO_2/N_2 2%
2623 CO_2/N_2 2.5%
2624 CO_2/N_2 3%
2625 CO_2/N_2 3.5%
2626 CO_2/N_2 4%

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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, 1981 in the Instrumentation Development 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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