NBS TECHNICAL NOTE 963

Air and Water Pollution

Annual Report FY 74-76

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

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Air and Water Pollution

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The NBS Air and Water Measurement Programs
(1974 - 1976)

William H. Kirchhoff
Eileen Myers

Abstract

This report contains a project by project description of progress and accomplishments in the National Bureau of Standards programs in air and water measurement covering fiscal years 1974 to 1976. These accomplishments include the development of new and improved methods for the measurement of substances in air and water, the development of standards for the testing and calibration of measurement methods and the provision of data for relating ambient air or water quality to emission or effluent levels.

The projects covered in this report deal specifically with:

Air--

Research leading to development of SRM's (Standard Reference Materials) or other means for ensuring the accuracy of air measurement methods.

Development of laboratory methods with improved accuracy, sensitivity and specificity for air pollution measurements.

Generation, evaluation, compilation and dissemination of data and technical information needed to relate the substances emitted from sources of pollution to those found in the atmosphere after chemical reactions have occured.

Water--

Evaluation of the accuracy of methods for measuring water velocity and flow in open and closed channels.

Development of radioactivity standards.

Development of Standard Reference Materials for evaluating the accuracy of instruments and methods for measuring the concentration of pollutants in water and sediments.

Measurement evaluation and compilation of physical and chemical properties of known pollutants.

Key Words: Air pollution; Measurement; SRM; Water pollution

Introduction

Measurement of the concentration and the chemical and physical properties of substances in air and water provides an understanding of the extent and effects of pollution. Without accurate measurement scientists cannot correctly relate health effects to levels of pollution, engineers cannot correctly assess the effectiveness of control techniques, regulatory agencies cannot correctly relate levels of pollution emissions with ambient air and water quality, and the government cannot correctly make policy decisions concerning compromises among the conflicting demands of environmental protection, energy conservation and economic health.

Although an element of uncertainty will always be present in understanding the environment, the purpose of the NBS programs in air and water measurement is to provide the means for quantifying and, where necessary, minimizing the uncertainty associated with assessing the extent and effects of pollution. It is important to emphasize the aspect of quantifying uncertainty. It is obvious that minimization of uncertainty cannot be demonstrated without quantification of uncertainty. Often, however, the environmental scientist has only vague estimates of the reliability of the numbers he obtains and it is rare to see reported environmental data accompanied by an estimate of accuracy. Without such an estimate, data has little significance for those who would later want to use it. High accuracy may not even be necessary so long as the limits of reliability of the data are known.

The objective of the NBS programs in air and water measurement is to provide the basis for determining the accuracy of air and water measurements and for achieving greater accuracy. This is accomplished through the development of improved measurement methods, the development of measurement standards and the provision of accurate technical information.

The NBS role in environmental measurement is derived from the Bureau's basic statutory responsibility for the accuracy and compatibility of measurements made throughout the Nation. The Clean Air Act of 1970 and the Water Pollution Control Act of 1972 direct the Administrator of the Environmental Protection Agency to cooperate with and encourage cooperative activities by all Federal departments and agencies having functions relating to the prevention and control of air and water pollution. This is to assure the utilization in the Federal pollution control program of all appropriate and available facilities and resources within the Federal Government.

Responsibility for management of the NBS air and water measurement programs rests with the Office of Environmental Measurement in the National Measurement Laboratory of NBS. Nearly 70 scientists from 12 technical divisions throughout NBS participate in the programs. The technical results of this effort are directed to a broad cross section of scientists and engineers in industry, Federal, State and local governments and private research institutions with responsibilities for and interests in environmental measurement. However NBS devotes nearly 1/3 of this effort to assisting other Federal agencies with special environmental measurement problems related to each agency's mission.

This report is a project-by-project description of the NBS Air and Water Measurement Program covering the fiscal years 1974-1976. In order to give a summary description of the program, the projects can be grouped into the following 10 categories:

Air Program

- Measurement Techniques for Trace Gases
- Standard Reference Material Development for Trace gases
- Measurement methods for Airborne Particulates
- Standard Reference Material Development for the Analysis of Particulates
- Atmospheric Chemistry Processes and Data

Water Program

- Standards and Guidelines for the Measurement of Water Flow
- Standards for the Measurement of Environmental Radioactivity
- Methods and Standards for the Measurement of Trace Levels of Inorganic substances in Water
- Chemical Processes and Properties Data

The following list is a summary of the major accomplishments of the air and water measurement programs during the fiscal years 1974-1976:

AIR PROGRAM

- Provision of reference materials to ASTM Project Threshold for collaborative tests of methods for SO_2, NO_2, sulfation, dustfall, airborne particles, lead and NO.
- Development of a high reliability exponential diluter as a dynamic gas calibration device.
- Development of Standard Reference Materials for quartz, toxic metals and 6 gases for the National Institute of Occupational Safety and Health for the analysis of hazardous materials in the work place.
- Provision of reference materials for a Collaborative test performed by the Environmental Protection Agency of a method for measuring CO in stack emissions.
- Development of an absolute coulometric method for measuring NO in NO_2.
- Development of gas blend Standard Reference Materials of CO in N_2 and NO in N_2. This completed the set of SRM's developed for automobile emission measurements.
- Demonstration of a piezoelectric technique suitable as a personal dosimeter for measuring mercury in air.
- Demonstration of a laser-Zeeman detector for NO.
- Demonstration of a fluorescence detector for NO.
- Demonstration of an acoustic delay technique for the measurement of automotive exhaust flow with a time resolution of less than 0.1 sec.
- Development of a prototype laboratory instrument for the Environmental Protection Agency for the determination of particle sizes by the measurement of the ratio of light scattering at two different forward angles.
- Issuance of an NO_2 permeation tube Standard Reference Material.

- Development of a thermal generator for trace concentrations of formaldehyde.
- Development for EPA of a "suitcase" blender for preparing known concentrations of SO_2 and CO for field calibrations of monitoring instruments.
- Development of reference materials for EPA for a national survey of vinyl chloride levels.
- Issuance of a lead-in-gasoline Standard Reference Material.
- Development of an infrared laser-Stark modulated detector for the measurement of specific gas phase pollutants and demonstration of the method for vinyl chloride.
- Measurement and characterization of the infrared spectrum of NO_2.
- Issuance of a report to Senate Labor and Public Welfare Committee on the adequacy of methods used to determine the exposure of coal miners to coal dust.
- Publication of evaluated chemical rate constants for reactions of importance in assessing the probable effects of atmospheric injection of oxides of nitrogen on the stratospheric ozone layer.
- Development and field-test of a prototype atmospheric sulfate monitor.
- Determination of the photochemistry and absorption cross-sections of Freon 11, Freon 12, and CCl_4.
- Measurement of the reaction kinetics of Freons and Freon substitutes with hydroxyl radicals using an NBS developed laser magnetic resonance detector.
- Workshop on Halocarbon measurements.
- Construction of a compact and stable CO_2 laser suitable for field instrument use in a spectroscopic detector for specific atmospheric constituents.
- Construction and evaluation of a laser Doppler spectrometer for characterizing the particle size distribution of aerosol generators and for calibrating particle sizing devices.

- Issuance of a stationary source SRM for SO_2.
- Workshop on Traceability of Calibration Standards.
- Development of a homogeneous urban particulate sample as a candidate SRM. The material was collected in a bag house located in St. Louis, Mo.
- Construction of a double-beam ultraviolet photometer as a primary standard for the accurate measurement of O_3 at concentrations typical of ambient levels.

WATER PROGRAM

- Publication of "A Guide to Methods and Standards for the Measurement of Water Flow".
- Conference on "Flow Measurements as Related to National Needs".
- Discovery of a technique for stabilizing ng/g concentrations of Hg in water and issuance of a trace mercury in water Standard Reference Materials.
- Construction of a water sampler with accompanying water sampling protocol for the analysis of ng/g concentrations of heavy metals in water.
- Preparation of an industrial river sediment Standard Reference Material certified for its trace metal composition.
- Characterization of transalkylation processes between tin and mercury.
- Development and test of a deep ocean sampler capable of retrieving water sample from a depth of 7 miles and maintaining the sample at its ambient pressure.
- Determination of the partition coefficients of 22 polycyclic hydrocarbons between air and water as a function of temperature and salinity.
- Development and verification of a theory for predicting the values of partition coefficients of aromatic compounds in water as a function of salinity from related Thermodynamic properties of these compounds.

- Development of a prototype monitor for the measurement of part per billion concentrations of chlorine in fresh and salt water.
- Workshop series on Standard Reference Materials needs for the analysis of pollution resulting from new sources and uses of energy.
- Development of a trace level multielement in water SRM.
- Development of a Standard Reference Material consisting of freeze-dried homogenized oyster tissue.
- Preparation of a report for the Federal Working Group on Pest Management on the testing and Evaluation of the Randers Meadows Model for the distribution of DDT in the Environment.
- Verification of a mathematical model for estimation of the effects of geometry and slope variations on the accuracy of Parshall Flumes for the measurement of water flow.
- Issuance of Environmental Radioactivity Standards including: Plutonium-239,242 Krypton-85, Xenon-133, Americium-243, Iron-55, Fresh Water Sediment and several mixed γ-ray solution standards.
- Publication for EPA of a Bibliography and summary of current literature on sampling, sample handling and long term storage for environmental materials.
- Development for The National Oceanic and Atmospheric Administration of techniques for the sampling and analysis of trace quantities of hydrocarbons in natural waters, sediments and tissues and publication of "Methods for Trace Hydrocarbon Analysis in the Marine Environment".
- Demonstration of a measurement method for organic derivatives of tin, arsenic, and selenium at nanogram levels.

The period covered by this report, fiscal year 1974-1976, culminated with the 8th Materials Research Symposium on Methods and Standards for Environmental Measurement. The five day symposium included over 100 contributed and invited presentations and attracted over 350 participants from government, industry and universities. The proceedings of this symposium have been published under the title "Methods and Standards for Environmental Measurements" and is available from the U.S. Government Printing Office, Washington, D.C. 20402. The stock number is 003-003-01704-03.

This introduction would be incomplete without mentioning that the Air and Water measurement programs during the 1974-1976 period covered by this report were under the leadership of James R. McNesby. Dr. McNesby led the programs since their inception as the "Measures for Air Quality" program in 1970. The outstanding accomplishments of the program are a direct consequence of his outstanding leadership. Also, during this period, Dr. Radford Byerly and Dr. Jimmie Hodgeson successively were responsible for the management of the air program and they must therefore also share in the responsibility for its success.

Finally, it should be noted that the entire report was typed by Ms. Carol Grabnegger, which may be responsible for her decision to begin a new career as a laboratory technician. Her patience and care are greatly appreciated.

William H. Kirchhoff
Eileen Myers

1. Automotive Exhaust Flowmeter

Project Leader: B. Robertson, Mechanics Division
Other Personnel: J. E. Potzick

Objective

The eventual, nearly instantaneous measurement of automobile exhaust pollutant concentration will require equally rapid measurement of total flow rate so that the mass rate of pollutant emission can be determined. The aim of this project is to develop and evaluate an essentially non-intrusive flowmeter for use along with pollutant detectors for measuring automotive pollutant emissions from the tailpipe. Rapidly varying flowrates averaging from about 13.6 to 204 g/s (11.3 to 350 ℓ/s), rapidly varying temperatures up to about 260°C, broadband noise levels up to more than 145 dB (re 2×10^{-5}Pa)[1], moisture, particulates, and corrosive contaminants are expected in the exhaust of a large automobile. For a small automobile, the average flowrate is expected to range from about 2.3 to 34 g/s (1.89 to 58 ℓ/s). Maximum permissible pressure drop is 200 Pa in order not to interfere with pollution control devices on the vehicle. One millisecond response time and one percent uncertainty are desired.

Approach

A number of closely related ultrasonic techniques have been evaluated. In all of them the meter consists of an approximately 5 cm diameter pipe connected to the end of the automobile tailpipe with acoustic waves beamed both upstream and downstream 5 cm or more through the flowing gas. The gas drags the sound in the direction of flow so that waves traveling upstream go slower, and waves traveling downstream go faster than when the gas is still. The resulting difference in transit times of the upstream and downstream traveling waves is obtained using microphones to detect the sound waves and an electronic circuit for processing. The time difference is directly proportional to the mass flowrate to be measured.

A new long wavelength version of this technique shows the greatest promise. In addition to the total mass flowrate, it provides a direct measurement of the average gas density so that the volume flowrate can be obtained.

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[1] Pa= Pascals= pressure drop

Progress

Six earlier ultrasonic techniques are described along with the reasons for their being discontinued. Finally the present long wavelength design is discussed in detail, and progress to date is reported.

The first technique involved placing two microphones equal distances upstream and downstream from a spark plug, which was on the opposite side of the pipe from the two microphones. The spark is fired, and the time interval between detection of the sound pulses is measured. Unfortunately, the spark jitters in space from one firing to another by an amount that leads to an uncertainty in the flowrate comparable to the flowrate to be measured.

The second technique involved replacing the spark by a specially made 1.5 cm diameter electrostatic tweeter. Unfortunately, the tweeter could not be made as loud as a spark, and hence had no hope of being heard over the exhaust noise.

The third technique involved replacing the spark by a 1.3 cm diameter 40 kHz piezoelectric transducer and measuring the phase difference between the ultrasound waves detected by the microphones. The pipe had to be made of the fibrous part of acoustic tile in order to minimize reflections, which confuse the measurement. This meter worked as long as the temperature was held constant.

The fourth technique involved setting the spark back from the pipe, and at the end of a 15 cm long, 4 mm diameter 'set back' tube connected to the pipe. This 'spark tube' method eliminated the spatial jitter of the sound source as did the second and third techniques above.

A subsequent theoretical analysis showed that all of the above 'divergent path' techniques would be sensitive to temperature gradients because different temperatures along the two paths would lead to an uncertainty in the flowrate which could be an unacceptably large fraction of the flowrate to be measured. Hence all later designs involved using a coincident path for the upstream and downstream traveling waves.

The fifth design involved two spark tubes and two microphones, one pair close together on one side of the pipe and the other pair on the other side and downstream of the first pair. The microphone adjacent to the end of a spark tube detects when the sound pulse is emitted from the tube, and the microphone across the pipe detects when the sound pulse arrives. For the other spark tube the roles of the microphones are reversed. The difference in transit times can be computed by using an up-down counter. This design was not constructed because of its complexity and because of the difficulty of producing a loud enough spark while also using sound absorbing walls in the tube in order to minimize reverberations and increase measurement repetition rate.

The sixth technique involved a 20 kHz and a 40 kHz piezoelectric transducers, each at the end of a set back tube in place of the two spark sources. The upstream and downstream waves could be distinguished because their frequencies were different. The phase shift of each of the upstream and downstream waves due to the dragging by the flowing gas was measured using the two microphones, and the difference in the phase shifts was computed using an up-down counter. This method worked substantially better than all previous ones. However, there were some unwanted reflections of the ultrasonic waves perhaps by the metal sound source tubes or by the imperfect sound absorbing walls of the pipe. The phase of these reflected waves changed with temperature, and hence their effect could not be cancelled electronically.

Long Wavelength Acoustic Flowmeter

The experience with the previous acoustic flowmeters has led to a new design which eliminates their undesirable features. In this design a loudspeaker driver at one end of the metering pipe generates a pure tone whose wavelength is longer than the diameter of the pipe. As a result only the fundamental sound mode can propagate, and higher modes generated at the driver and by irregularities in the pipe wall will be quickly damped. Hence, the entire sound field inside the meter can be known at all temperatures even though no sound absorbing material is used.

Another important advantage of using long wavelength sound is that the flow measurement will be independent of the details of the spatial dependence of the local gas flow velocity and density, and depend only on the total mass flowrate and the average of the density over the cross section of the pipe. This has been proved using the equations of mass, momentum, and entropy conservation of an ideal fluid by using perturbation technique,[1] and correction terms have been obtained,[2] which are small for the present flowmeter design. This profile-independent flowmeter is highly desirable since its indication for a given actual flowrate will not vary from car to car because of differences in muffler and tail pipe configuration.

The sound is detected by three 3.2 mm diameter condenser microphones mounted 15 cm apart on one side of the pipe with their diaphrams nearly flush with the inside surface of the pipe. The only part of the signal from the microphones that is needed is the zero or null of the sound wave, since null time differentials determine the gas velocity (see below). As a result, the flow measurement does not depend on the microphone gain, which changes somewhat at higher temperatures.

As the temperature and hence the speed of sound in the exhaust gas changes, the frequency of the sound is changed automatically to maintain the wavelength equal to the spacing between the first and third microphone. This simplifies the determination of the flowrate so that it is obtained by measuring a time interval as before. Now, however, the gas density also can be obtained by measuring the sound frequency.

Theory of Operation

The sound field consists of two oppositely traveling waves because of reflection of the sound at the end of the pipe. This field is a function only of longitudinal positional x and time t of the form

$$p(x,t) = A_+ \cos\left(\omega t + \frac{\omega x}{\bar{c} - \bar{v}} + \phi_+\right) + A_- \cos\left(\omega t - \frac{\omega x}{\bar{c} + \bar{v}} + \phi_-\right), \qquad (1)$$

where p is the acoustic pressure, $\omega/2\pi$ is the frequency, $\bar{c}$ is the effective speed of sound, $\bar{v}$ is the mean exhaust velocity to be measured, and A_+ and ϕ_+ are constants. The quantities $\bar{c}$ and $\bar{v}$ are given, for $\bar{v}/c \leq 1/10$, by[1,2]

$$\frac{1}{\bar{c}^2} = \frac{\langle\rho\rangle}{\gamma p} \quad ; \quad \frac{\bar{v}}{\bar{c}^2} = \frac{\langle\rho v\rangle}{\gamma P}, \qquad (2)$$

where γ is the ratio of specific heats, P is the barometric pressure, ρ is the local gas density, v is the local gas flow velocity, and the angular brackets denote an average over the cross section of the pipe. The averages $\langle\rho\rangle$ and $\langle\rho v\rangle$ are related to the total mass flowrate G and volume flowrate Q by

$G = \langle\rho v\rangle A$, $\quad Q = \langle\rho v\rangle A/\langle\rho\rangle$, $\quad$ where A is cross-sectional area of pipe.

Hence, $\bar{c}$ and $\bar{v}$ that appear in the expression for the sound field depend only on known quantities, like γ and P etc., and on the G and Q to be measured.

Let t_i and t_j be the zero-crossing times of the microphones at longitudinal positions x_i and x_j, where i, j = 1,2, or 3. Application of trigonometric identities to Eq (1) gives, to first order in $\bar{v}/\bar{c}$,

$$\frac{\bar{v}}{\bar{c}^2} = \frac{n\pi/\omega + t_i - t_j}{x_j - s_i} - \frac{1}{\omega}\,\frac{\tan^{-1}\Theta_{ji}}{x_j - s_i}, \tag{4}$$

$$\Theta_{ji} \equiv \frac{(A_+^2 - A_-^2)\sin[\omega(x_j - x_i)/\bar{c}]}{(A_+^2 + A_-^2)\cos[\omega(x_j - x_i)/\bar{c}] + 2A_+A_-\cos[\omega(x_j + x_i)/\bar{c} + \phi_+ - \phi_-]} \tag{5}$$

and n is an integer, which we can choose to be zero. The frequency $\omega/2\pi$ is chosen so that the spacing ℓ between microphones satisfies.

$$\ell = \pi\,\frac{\bar{c}}{\omega} = \frac{\lambda}{2}, \tag{6}$$

where $\ell = x_2 - x_1 = x_3 - x_2$ and λ is the wavelength. Then $\Theta_{ji} = 0$, and Eq (4) is substantially simplified. Since ℓ = 15 cm, $\bar{c}$ - 332 m/s at 0°C, and c^{-2} is proportional to the absolute temperature, the frequency $\omega/2\pi$ satisfying Eq (6) ranges between 1090 and 1520 Hz.

The expressions for the total mass and volume flowrates obtained by combining Eqs (3), (2), (4), and (6) are

$$G = \gamma PA\,\Delta t/\ell, \tag{7}$$

$$Q \pm \frac{\omega^2 A}{\pi^2}\,\ell\,\Delta t, \tag{8}$$

where $\Delta t = t_1 - t_2 = t_2 - t_3$. Now the area A and length ℓ are known, the barometric pressure P can be measured, and the specific heat ratio varies slowly with temperature and equals 1.37 for dirty exhaust, 1.38 for clean exhaust, and 1.39 for humid or dry air. Hence, the total mass flowrate G can be obtained from a measurement of the time interval

Δt. Also, the volume flowrate Q can be obtained from Δt and the frequency $\omega/2\pi$ and does not depend upon γP.

In order for the flowmeter to be able to determine the frequency that satisfies Eq (6), it must obtain the difference in time differences: $\Delta^2 t \equiv (t_2 - t_3) - (t_1 - t_2)$. For frequencies that nearly satisfy Eq (6), we find from Eqs (4) and (5) that

$$\Delta^2 t = \frac{A_+{}^2 - A_-{}^2}{\omega} \quad \frac{4A_+A_-\sin(\phi_+ - \phi_-)}{[A_+{}^2 + A_-{}^2 + 2A_+A_-\cos(\phi_+ - \phi_-)]^2} \quad \left(\frac{\omega\ell}{c} - \pi\right)^2 \tag{9}$$

where we have chosen the origin so that $x_2 \equiv 0$. The correct frequency is obtained when $\Delta^2 t$ is zero. Since $\Delta^2 t$ is a function of the frequency deviation squared, the frequency must be dithered

$$\omega = \omega_0 + \omega_1 \sin \omega_d t \tag{10}$$

with $\omega_d << \omega_0$ to determine whether to increase or decrease the frequency in order to set $\Delta^2 t$ equal to zero.

Since the response time of the frequency adjusting circuit must be slower than $2\pi/\omega_d$, the above inequality states that the response time of the flowmeter must be much slower than 1 ms. However, this response time refers only to flow transients, e.g. due to engine acceleration, the effect of flow pulsations due to individual cylinder firing is not presently known.

Construction and Testing

A long wavelength flowmeter consisting of the three microphones, a loudspeaker driver, and a simplified, bread boarded electronic circuit has been constructed. In this version the frequency was adjusted manually to get the right wavelength. Preliminary tests with heated air flowing through the meter pipe show that the basic physical principles described above are qualitatively confirmed.

A block diagram of the proposed complete flowmeter circuit[3] is in Fig 1.1 The upper half consists of three channels, one for each microphone, and circuits for obtaining the time diferences $t_1 - t_2$, $t_2 - t_3$, and $t_1 - t_3$. The last of these is used for the flowmeter output, which is proportional to the total mass flowrate. The lower half of the circuit adjusts the frequency of the sound so that the wavelength is held equal to 2ℓ.

One of the most important parts of the flowmeter circuit is the synchronous zero-crossing marker. This is a specially designed[4] narrow-banding circuit, which uses a phase sensitive detector, an integrator, and a voltage controlled phase shifter, all in a feedback loop. The circuit converts a voltage consisting of a sinusoidal signal plus noise into a clean square wave whose zero crossing accurately marks the instant when the sinusoidal signal (without noise) crosses zero. This circuit substantially reduces the jitter in the measurement of the zero crossing time. The resulting jitter is given by

$$(\delta t_i)_{rms} = V_n/(\omega V_s\sqrt{\Omega\tau}), \tag{11}$$

where V_n is the rms noise voltage of bandwidth $\Omega/2\pi$, V_s is the rms signal amplitude, and τ is the response time of the circuit. Hence the time jitter can be made arbitrarily small by slowing the response time.

This circuit has been constructed. Tests on it indicate that it performs as described. If we assume $V_s/V_n = 10$, $\Omega/2\pi = 150$ kHz, and $\tau = 1$ ms, the time uncertainty $(\delta t_i)_{rms}$ will be 500 ns. The same uncertainty results from a less piercing signal-to-noise voltage ratio of 1 provided the response time is slowed to 100 ms.

The 500 ns zero-crossing-time uncertainty causes an uncertainty in the flow measurement. Since $v_{max}/\bar{c} = 1/10$, Eqs (4) - (6) give a velocity uncertainty of 1 percent of full scale. Because of Eq (3), this gives a flowrate uncertainty also 1 percent of full scale. Since the noise will decrease with decreasing flowrate, the uncertainty may be expected to decrease also and remain approximately a constant 1 percent of reading.

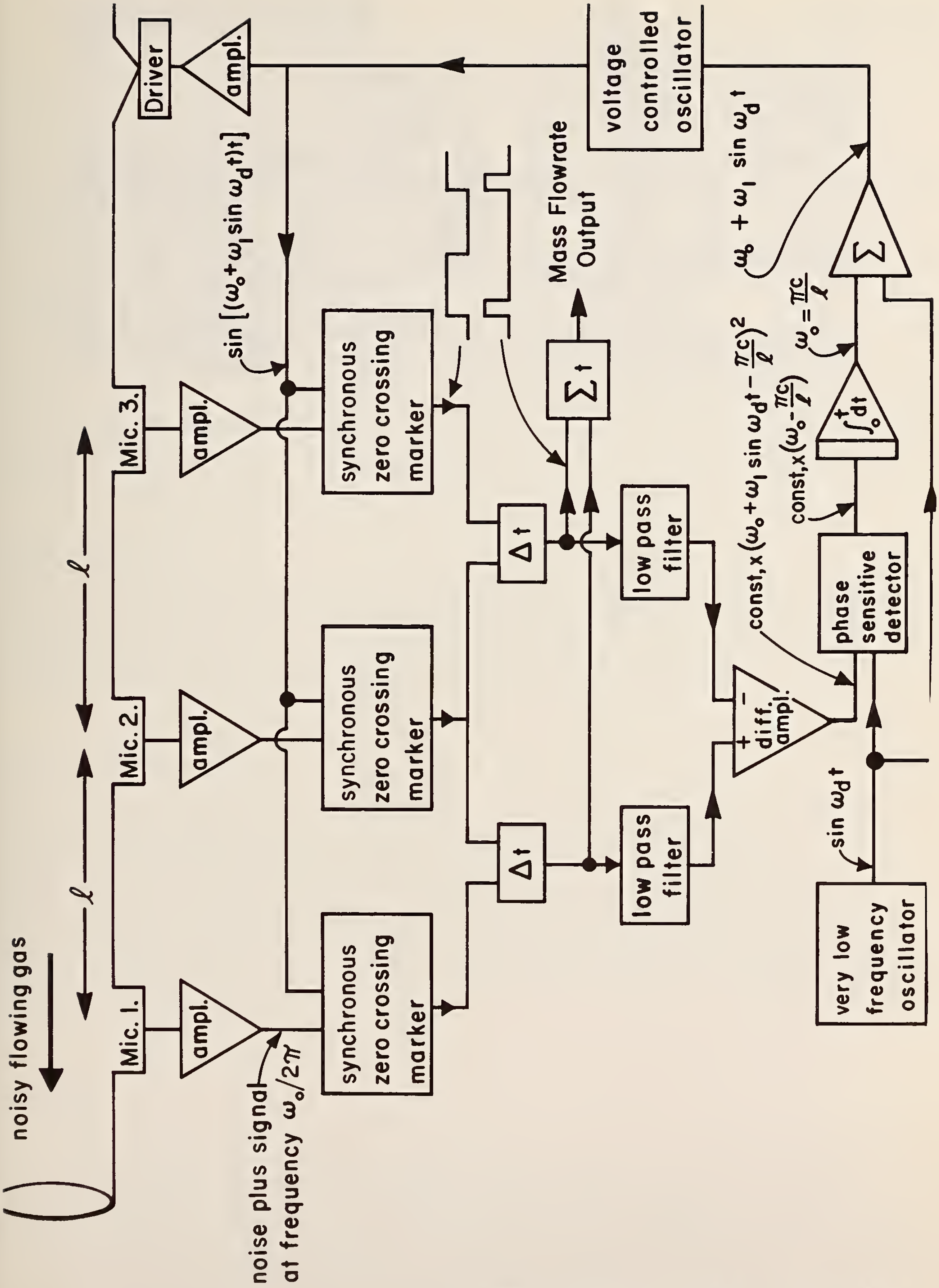

Figure 1.1 Long Wavelength Acoustic Flowmeter

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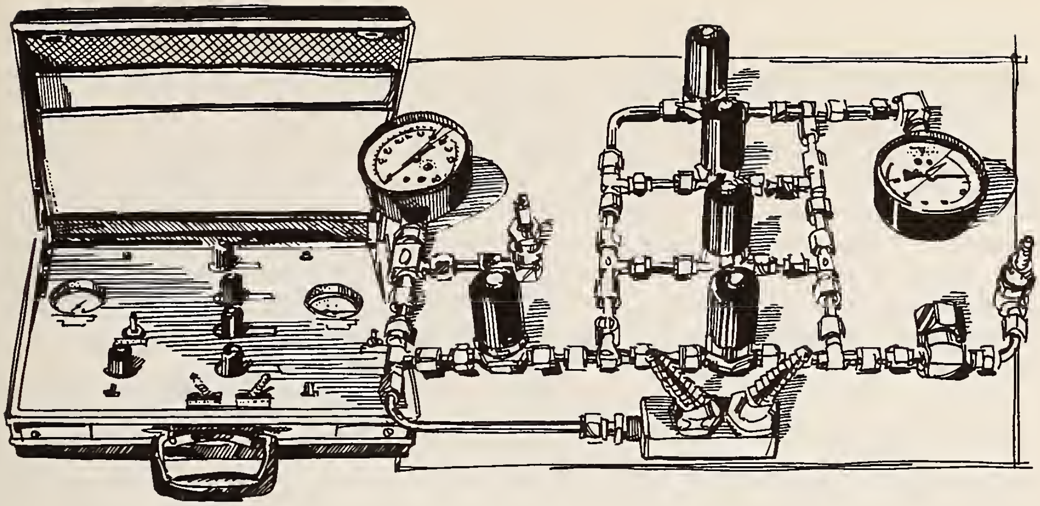


2. Building and Evaluation of a Polluted Air Delivery System

Project Leader: G. P. Baumgarten and F. W. Ruegg, Mechanics Division

Objective

This report describes the building and evaluation of a prototype SO_2 polluted air delivery system (PADS). This system is intended for field use with performance specifications prescribed by the Environmental Protection Agency.

Approach

The delivery system was built to deliver sulfur dioxide (SO_2) in air at a rate of 5 liters per minute with design concentrations by volume of 1.0, 0.1 and 0.01 parts per million. It consists of a diluent air delivery system utilizing a critical flow sonic nozzle and three separate concentrated SO_2 in air flow systems utilizing laminar flow porous plugs, one plug for each desired output concentration (Figure 2.1).

Progress

As seen in the sketch the delivery system is contained in a dispatch case and the two gases are delivered to it from pressurized containers through detachable supply lines. Prospective use by unskilled technicians dictated simplicity, durability and compactness. By maintaining specific upstream pressures on the critical flow nozzle and the laminar flow porous plugs of 45 and 12 psig respectively, the prototype

PADS produced average output concentrations of 0.76, 0.100 and 0.003 parts per million of SO_2 in air based on concentration measurements with an NBS calibrated analyzer. The expected output concentrations were 0.98, 0.105, and 0.010, respectively, based on flow calibrations of the individual components. The uncertainty of the output concentration is estimated to be about ± 10 percent. A detailed description of the system is to be found in NBSIR 73-414, April 1974. This work was supported by the Environmental Protection Agency.

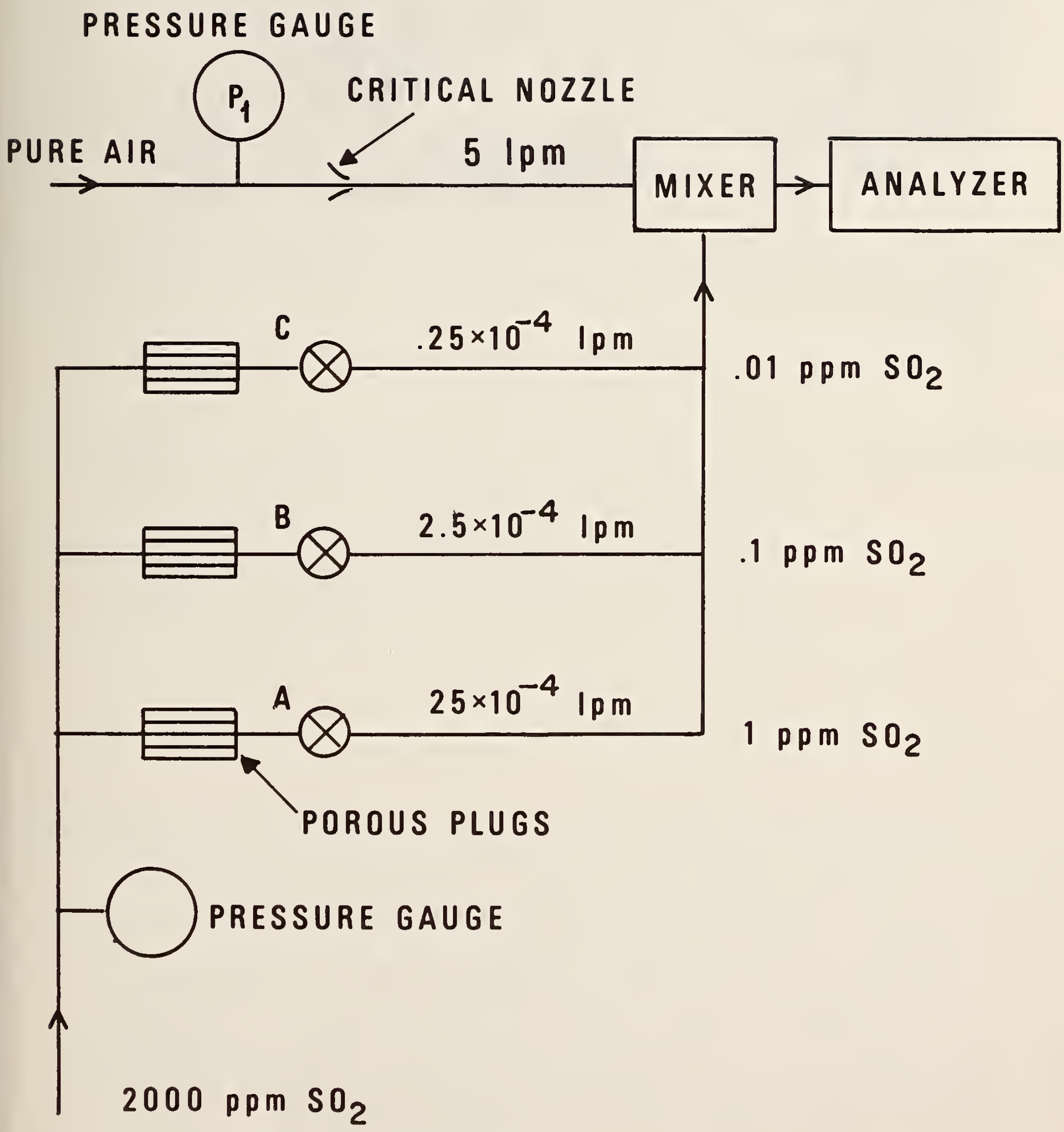
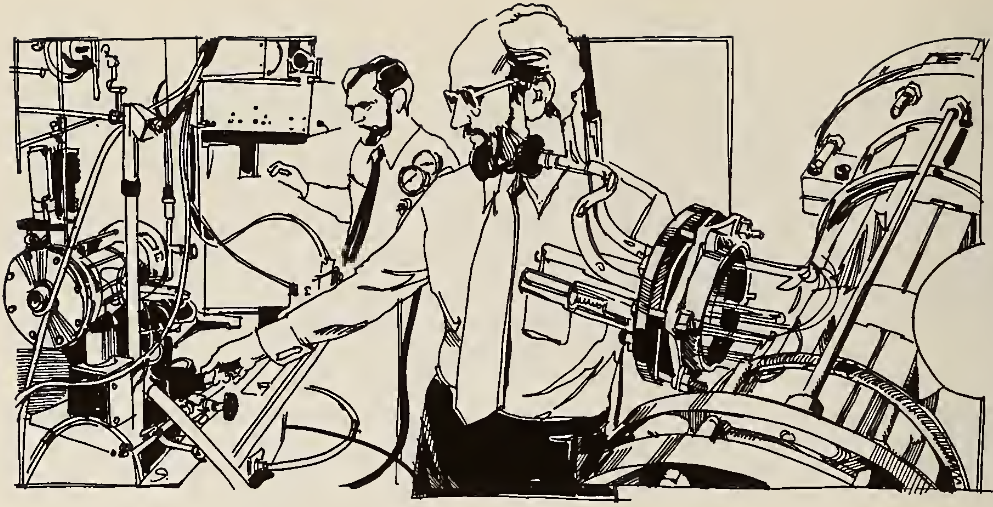


Figure 2.1 Polluted Air Delivery System.



3. Applications of Infrared Measurements to Air Pollution Problems

Project Leaders:	R. Deslattes, Optical Physics Division, C. J. Howard, NOAA
Other Personnel:	H. E. Radford, W. J. Lafferty, S. Freund, H. Layer, P. Schenck, J. Hougen, A. Maki, Optical Physics Division; Y. Beers, K. Evenson, J. S. Wells, Time and Frequency Division; J. Devoe, D. Sweger, E. Hughes, Analytical Chemistry Division; H. Okabe, Physical Chemistry Division, and G. E. Streit, NOAA

Objective

To develop techniques and supporting information for measuring spectroscopically the concentrations of various molecules which play a role in air pollution. Currently emphasis is being placed on measuring and analyzing the spectra of NO_2, O_3, OH and HO_2. The latter two molecules are critical species in the chemistry of both smog formation and stratospheric ozone destruction by anthropogenic pollutants. The vital necessity of understanding its chemical kinetics requires the development of a quantitative method for its measurement. This broad project has brought together in concert resources of 4 NBS Divisions and one sister agency (NOAA).

Approach

Techniques and instrumentation are developed to utilize ultraviolet and infrared laser devices in measuring air pollutants. In order to expand the versatility and specificity of fixed frequency molecular lasers, absorption modulation techniques such as the Zeeman and Stark effects are being investigated. As additional back-up data the high resolution absorption characteristics of NO_2, O_3, and HO_2 are being studied. These techniques exploit the near coincidence of a particular transition in a molecular laser such as CO with an absorption feature in the spectrum of a pollutant molecule. If the latter is paramagnetic, its absorption can be brought into coincidence with the laser emission by the application of a magnetic field (Zeeman effect). If the pollutant is polar, an electric field can be used for the same purpose (Stark effect). Continuously tunable IR lasers such as the spin-flip Raman laser are also used to measure specific pollutant species.

3.1 Laser-Zeeman Spectrum of HO_2

Using a Zeeman-modulated cavity spectrometer with a 10 s time constant and a phase locked klystron, HO_2 Zeeman components of the six allowed zero-field lines at 65,070 ± 2, 65,082±2, 65,098 ± 2, 65,373 ± 2, 65,397 ± 2, and 65,401 ± 2 MHz, and of one forbidden zero-field line at 65,369 ± 4 MHz, have been observed in the products of a discharge-flow system[1] The Q of the Fabry-Perot cavity is about 10,000, and the magnetic field was swept from 0 to 30 gauss. Chemical tests indicate that the observed lines are due to HO_2. They have been assigned and least-squares fitted using a simple theoretical model, to yield a value of 65,185 ± 2 MHz for the $1_{01}-0_{00}$ asymmetric rotor transition frequency of HO_2, a value of -208 ± 2 MHz for the linear combination $1/2\ (\epsilon_{bb} + \epsilon_{cc})$ of elements of the electron spin-molecular rotation interaction tensor, a value of -28 ± 2 MHz for the nuclear spin - electron spin Fermi contact interaction parameter, σ, and a value of +4 ± 2 MHz for the spin-spin tensor interaction parameter, λ.

The analysis of the laser magnetic resonance spectrum of HO_2 has been published[2,3] Experiences gained while working on the details of the HO_2 spectrum have been generalized and have led to the publication of a paper[4] containing a straightforward and logical, though somewhat lengthy, prescription for analyzing any future data from laser magnetic resonance spectrometers (e.g. that measured for NO_2).

Figure 3.1.1 shows a plot of Zeeman energy levels for HO_2 versus applied magnetic field. The circles, squares, and triangles indicate allowed laser magnetic resonance transitions of the three types M=0, 1. Diagrams of this nature, though complicated, have proven to be of great help in visualizing the relationship between observed spectra and theoretical molecular energy level patterns.

Table 3.1.1 gives the zero-field asymmetric rotor energy levels (E) obtained to date for HO_2 from the magnetically shifted Zeeman spectra, and gives a good indication of the significant extent of our present knowledge. The column of observed-calculated values (0-C) indicates the quality of our theoretical understanding of the data.

Table 3.1.2 gives a set of rotational constants for the HO_2 molecule obtained from the asymmetric rotor energy levels in table 3.1.1 as well as a comparison with rotational constants obtained from *ab initio* calculations (SCF and CI). Discussions with the *ab initio* people indicate that they do not expect any better agreement with experiment than that shown in the table.

Table 3.1.1

Zero-Field Asymmetric Rotor Energy Levels (E) for HO_2

HO_2 ASYMMETRIC ROTOR FIT (A, B, C, D_K, D_{NK}, D_N)

$N'(K'_a,K'_c)$	-	$N''(K''_a,K''_c)$	E[cm^{-1}]	O-C [cm^{-1}]
7(2,6)	-	7(1,7)	58.587	+0.000
8(2,7)	-	8(1,8)	58.833	+0.006
11(2,9)	-	10(1,10)	83.380	-0.002
12(2,10)	-	11(1,11)	85.923	+0.002
13(2,12)	-	12(1,11)	83.531	-0.002
14(2,13)	-	13(1,12)	85.291	-0.004
15(2,13)	-	14(1,14)	93.782	-0.006
4(3, 1)	-	5(2, 4)	85.207	-0.001
4(3, 2)	-	5(2, 3)	85.201	-0.002
10(3, 8)	-	9(2, 7)	117.696	-0.007
10(3, 7)	-	9(2, 8)	117.750	-0.002
11(3, 9)	-	10(2, 8)	119.852	+0.009
11(3, 8)	-	10(2, 9)	119.926	+0.011
14(3,12)	-	13(2,11)	126.198	-0.012
14(3,11)	-	13(2,12)	126.404	-0.007
15(3,13)	-	14(2,12)	128.320	+0.009
15(3,12)	-	14(2,13)	128.588	+0.008
18(4,14)	-	19(3,17)	92.664	-0.000
18(4,15)	-	19(3,16)	92.647	-0.001

Table 3.1.2

HO_2 ROTATIONAL CONSTANTS [cm^{-1}]

	This Work	SCF[a]	CI[a]
A	20.357	21.368	20.576
B	1.117 6	1.035	0.938
C	1.056 4	0.987	0.897
Δ_K	0.004 1		
Δ_{NK}	0.000 117		
Δ_N	0.000 000 5		
σ	0.007 4		

[a] Liskow, Schaefer and Bender, JACS 93, 6734 (1971)

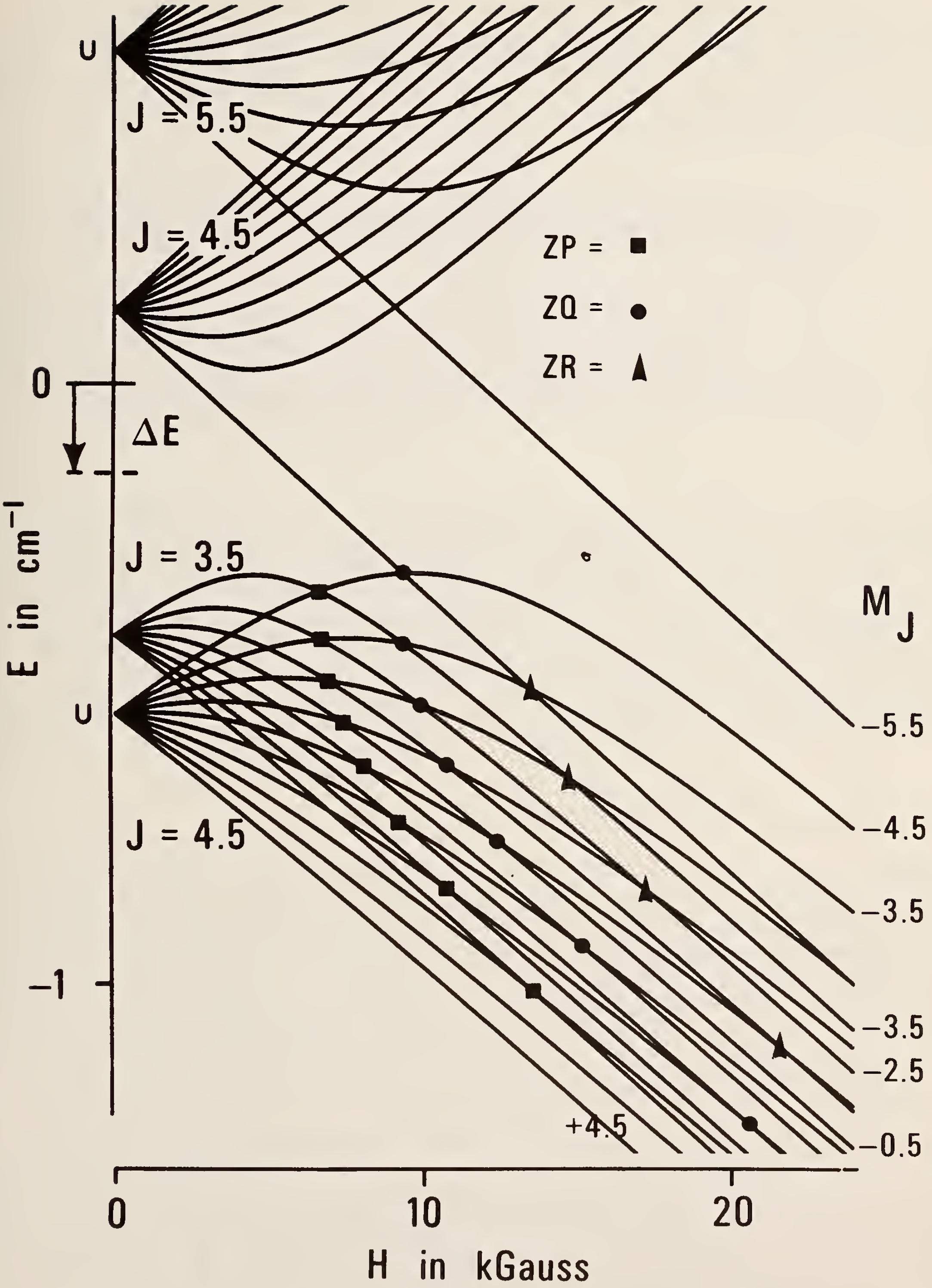


Figure 3.1.1. Zeeman Energy Levels of HO$_2$ and Magnetic Resonance Transitions

The work described above is quite significant, both for the information which it has produced on the important free radical HO_2, and because it systematizes and simplifies data interpretation from the new and sensitive technique of laser magnetic resonance spectroscopy.

3.2 Rate Constants for the Reactions of OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K

The absolute rate constants for the reactions of OH radicals with CH_4 and fifteen fluorine, chlorine, and bromine substituted methane molecules have been measured using a discharge flow system and laser magnetic resonance detection of OH. Measurements were made at 296 K and at pressures between 0.8 and 1333 Pa.

The results indicate that the reaction mechanism involves the abstraction of a hydrogen atom and formation of H_2O and a methyl type radical product. Completely halogenated methane molecules are found to be relatively unreactive. Hydrogen containing molecules react with rate constants ranging from about 0.2 to 160 x 10^{-15} cm^3/molecule·sec. The reactivity increases with decreasing carbon-hydrogen bond energies. Rough estimates are made of the Arrhenius parameters for the reactions.

3.3 Spectral Measurements on NO_2

We have nearly completed high resolution measurements of the entire infrared spectrum of NO_2.[5-9] The main thrust of the measurements was to present a complete set of measurements on the strongest absorption bands, but work was necessary on all the bands in order to aid in the analysis of the most important bands. The first analysis of the most important band (ν_3 at 1617 cm^{-1}) was the subject of a joint publication with Prof. K. N. Rao and Dr. S. C. Hurlock of Ohio State University.[6] In order to improve on those measurements we have collaborated with Prof. A. Cabana of the University of Sherbrooke to publish measurements with a four-fold improvement in resolution.[9] This work on the ν_3 band has been used elsewhere to produce a computer synthesized spectrum to simulate the spectrum of NO_2 expected in upper atmosphere measurements. Such synthesized spectra are vital to the interpretation of spectra obtained from instrumented balloon flights.

Some laser Zeeman spectra of the ν_3 band of NO_2 were also measured[10] and it was found that several absorption lines are easily Zeeman shifted into resonance with CO laser transitions. Two laser magnetic resonance patterns for $^{14}NO_2$ and six patterns for $^{15}NO_2$, observed using six CO laser transitions, have been analyzed to yield spin-corrected Zero-field vibration-rotation transition wavenumbers and zero-field spin-rotation splittings. The planning and analysis of the laser Zeeman measurements was aided by the earlier analysis of the ν_3 band obtained from the conventional infrared grating studies made in this laboratory. The results from both the laser and the grating techniques are in good agreement. The $^{15}NO_2$ results allow new values of $\nu_0 = 1582.107 \pm 0.008$, $A'-A'' = 0.2116 \pm 0.0011$, and $D_K' - D_K'' = 1.39 \pm 0.20 \times 10^{-4}$ cm^{-1} to be determined for the ν_3 fundamental of that molecule (errors are 3 standard deviations).

3.4 Measurement and Analysis of the IR Spectrum of Ozone (O_3)

The second strongest absorption band of ozone ($\nu_1+\nu_3$) has been measured and a complete analysis of all the strongest transitions is finished. An atlas giving line wavenumber measurements and quantum number assignments has been published.[11] The line atlas includes a reproduction of the spectrum to indicate the relative intensities of the different lines. An expanded version of the spectrum has already been used to identify ozone absorption lines in spectra of the earth's atmosphere recently taken at Kitt Peak Observatory.

3.5 Laser-Stark Spectroscopy

A Stark cell was constructed for use in conjunction with various fixed frequency molecular lasers for measuring the concentrations of pollutants such as formaldehyde, ozone, and vinyl chloride. Analytical measurements of vinyl chloride in air have been performed on samples ranging from 0.1 ppm to 1000 ppm. The sensitivity and linearity over the entire range produced good results which have been published. [12]

The results of this early work showed that concentrations as low as 2 ppm could be measured. Preliminary checks for accuracy were made using gas mixtures of VCM (vinyl chloride monomer) in air provided by E. Hughes of the Air and Water Pollution Analysis Section. Linearity of signal vs concentration was established from 2 ppm to over 1000 ppm. Subsequent improvements in measurement techniques have extended the sensitivity to approximately 0.1 ppm. These results were presented at the Pittsburgh Conference in April 1975 and are shown in Figures 3.5.1 and 3.5.2 . Figure 3.5.1 is a reproduction of actual X-Y plotter traces taken from the digital oscilloscope used for signal averaging and are included to demonstrate the S/N ratios. The approximate averaging times range from 20 s at 95 ppm to 20 min at 0.1 ppm. Figure 3.5.2 shows the analytical curve obtained and contains the results of three runs taken over a period of several days. Note that the scale is folded and that the data are normalized to the 9 ppm sample. Much of the earlier work was normalized to the 27 ppm sample and is not shown here.

Some progress has been made in looking for interferences. A list of chemicals most likely to be found in an industrial atmosphere containing VCM was compiled and most of these chemicals have been obtained. Of the dozen or so chemicals that have been scanned with the CO_2 laser to date there are no serious interferences with the exception of acrylonitrile, which exhibits a very strong absorption on the same CO_2 laser line as does VCM. It should be noted, however, that acrylonitrile also strongly absorbs laser lines that VCM does not, and further that there should be no interference between these two in the CO laser region. Some interference experiments show that several chemicals are strong absorbers of CO_2 laser emissions other than that used for VCM. These experiments show promise of the extension of this detection scheme to other important chemicals.

3.6 Ozone Kinetics Studies

Some kinetics studies have been completed on the reaction of vibrationally excited ozone with NO, a reaction which may be of significance to upper atmosphere chemistry [13,14]. Results include measurements of the rate coefficients for the reactions of vibrationally excited ozone with NO, SO, and $O_2(^1\Delta)$. Rate enhancements have also been observed in the reaction with O atoms. The laser enhanced chemiluminescent reaction with NO has been used to monitor the rate of deactivation of vibrationally excited O_3 with He, Ar, H_2, N_2, O_2, H_2O, CO_2, SO_2, CH_4, and SF_6. From this study it was possible to separate reactive from deactive processes. Further, it was shown that the activation energy for O_3^* + NO reaction was identical to that of ground state ozone + NO reaction indicating that vibrational energy requires a given translational energy in order to couple to the reaction coordinate leading to activated complexes. Further work completed during FY 1975 includes the effect of vibrational energy on the O + OCS and O + C_2H_4 systems. While these two systems are not of

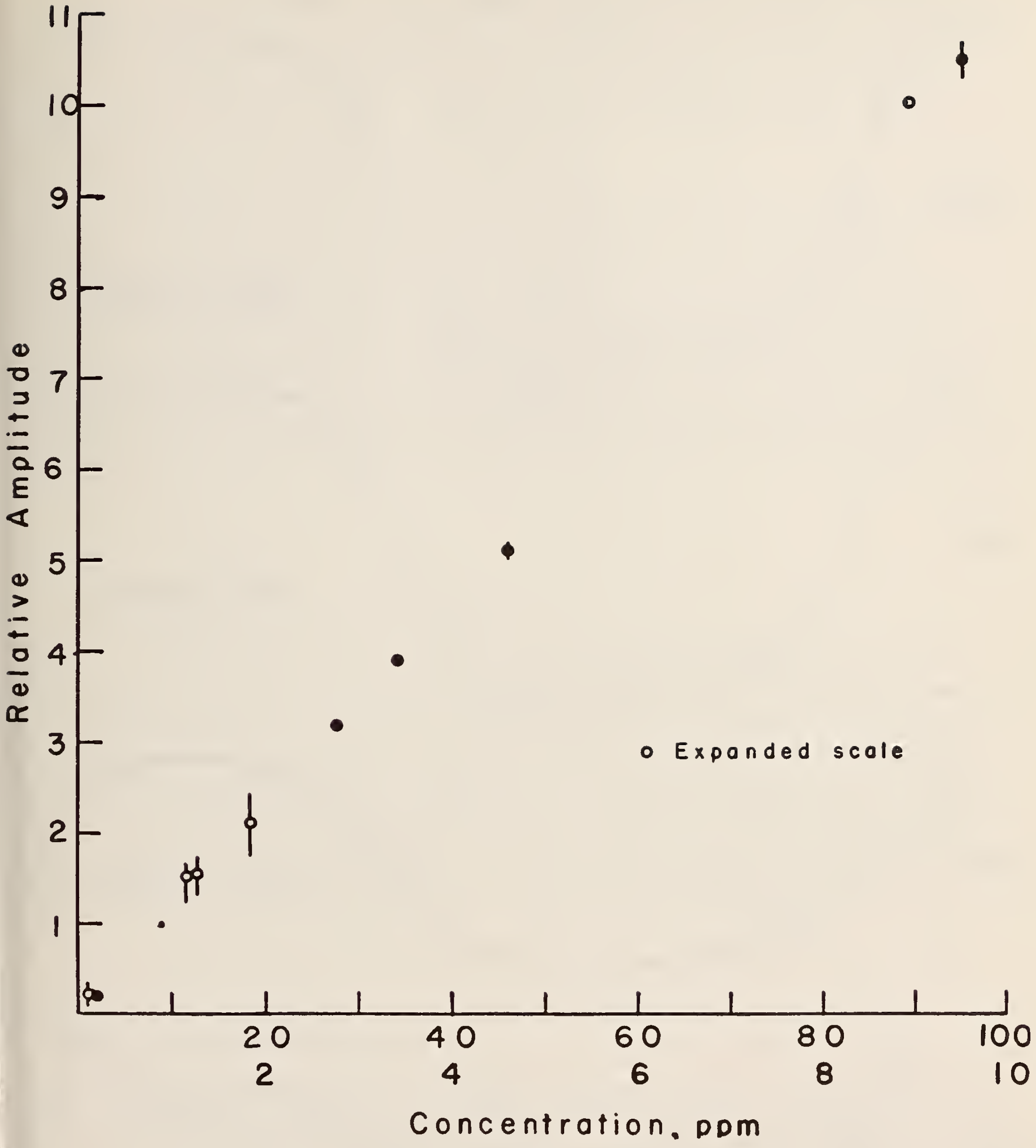


Figure 3.5.1 X-ray plotter traces from the digital oscilloscope used for signal averaging

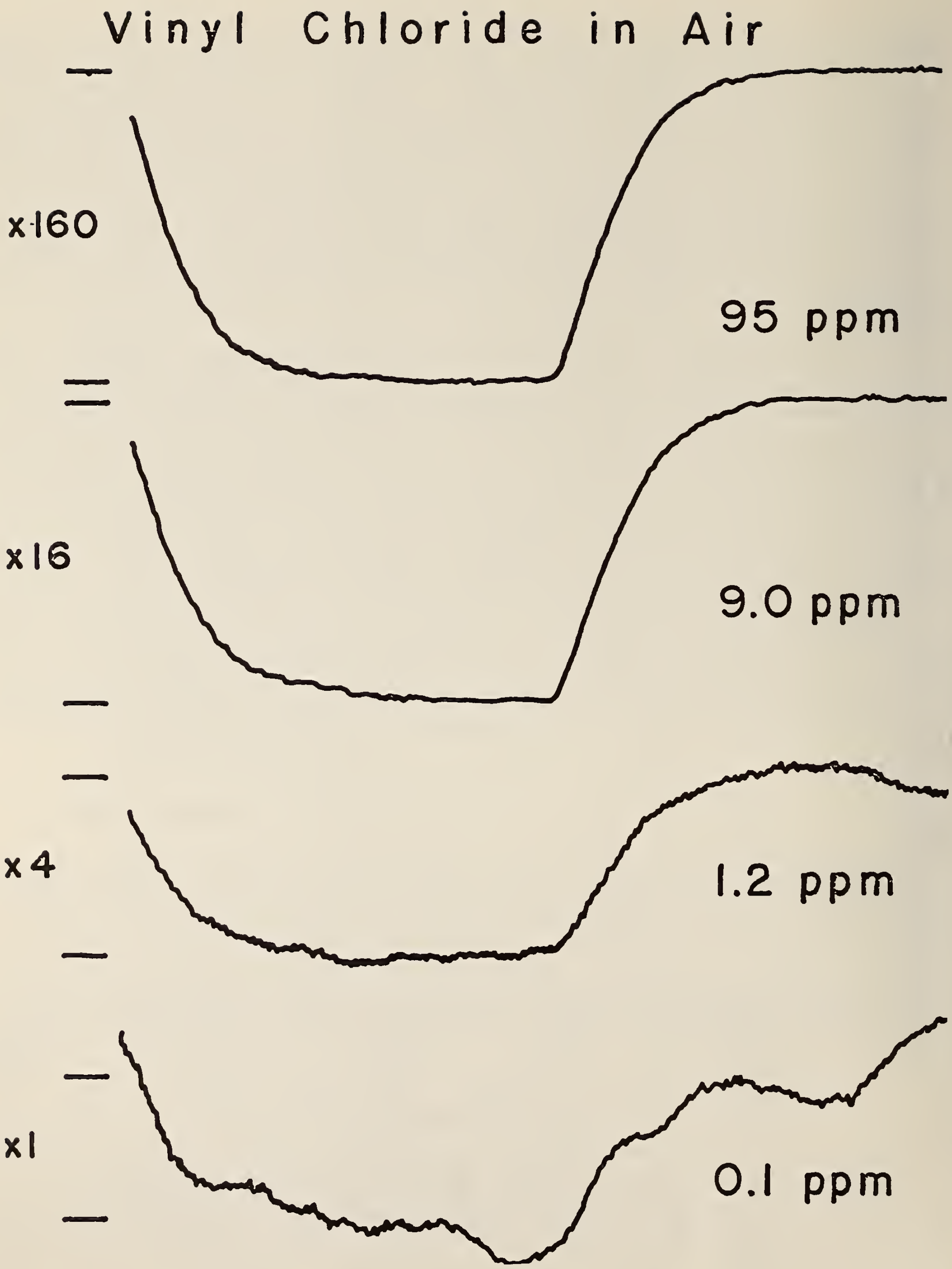


Figure 3.5.2 Analytical curve and results of three runs of vinyl chloride in air.

atmospheric interest they do help in testing models for predicting the effect of vibrational energy on chemical dynamics. Current studies are underway to measure the rate constant for the O + ClO reaction because of its involvement in stratospheric chemistry, and to investigate the rates of reactions of Cl atoms with ground state, vibrationally excited molecules, specifically of atmospheric interest.

Also, a CO laser was used to pump optically the first vibrational level of nitric oxide, NO (v=1). In a fast flow, chemical reaction cell the rate constant for the reaction $NO(v=1) + O_3 \xrightarrow{k_1'} NO_2\ (^2B_2) + O_2$ was measured. This constant was compared to the corresponding rate constant for vibrationally unexcited reactants $NO(v=0) + O_3 \xrightarrow{K_1} NO_2\ (^2B_2) + O_2$ with the result that $K_1'/K_1 = 2.7$. Since the N-O bond does not break during the collision leading to chemical reaction between NO and O_3, it was somewhat surprising that the rate constant was so increased. This is the first direct demonstration that vibrational excitation in a non-reactive bond enhances chemical reactivity.

3.7 Sulfur Dioxide Fluorescence

Work on fluorescence of SO_2 using a doubled nitrogen laser pumped dye laser in order to determine the optimum laser wavelength for use in SO_2 monitoring has been completed. The combination of doubling efficiency with available doubling crystals and the fluorescence quantum yield indicated that 220.5 nm is the optimum wavelength for SO_2 monitors using laser induced fluorescence. Fluorescence from the 220.5 nm band could easily be observed at 2 ppm ($S/N > 20$) in air in an apparatus designed primarily for spectroscopic investigations. The indications are that laser induced fluorescence should enable monitoring of SO_2 at ppb level in a suitable apparatus.

3.8 Wave Guide Lasers

The performance of several high pressure CO_2 wave guide lasers, which had been constructed during the previous reporting period, have been extensively studied. In addition to their primary asset of being widely tunable (over an order of magnitude greater than conventional CO_2 lasers) they exhibit unexpectedly high amplitude and frequency stability. While this inherent stability is not completely understood, it does result in part from the short sturdy construction of the laser cavity. These lasers are being used in a study of the saturated absorption spectroscopy of SiF_4 which will help define the limits of concentration and specificity over which such a system will be useful.

3.9 Tunable Semiconductor Laser Applications

A second generation spin flip Raman laser has been completed. The new system consists of an electromagnet whose field and sweep parameters are selected by a commercial field dial controller. The magnetic field range is 0-1 tesla (0-10 k gauss). A liquid helium dewar with provisions for either cooling by a cold finger or immersion in liquid helium is in use. A new CO pump laser of improved design was constructed. This new laser operates between 1900 and 1700 cm^{-1}. This laser may be frequency stabilized by locking it to a reference synthesized from a CO_2 laser and a kystron. We now have three different concentrations to choose from for the InSb resonator. With the second generation system, the operating range has been extended to between 1900 and 1800 cm^{-1}. The spectroscopic capabilities of the 2nd generation SFRL and the opto acoustic detector are indicated in an NBS Tech Note .[15] More recently, infrared frequency synthesis techniques with metal-insulator-metal diodes have led to absolute frequency measurements with our SFRL system.

The molecule of greatest interest at present is HONO, and the SFRL frequency coverage has <u>not</u> been extended to the band of interest at 1696 cm^{-1}, thence a brief investigation as to the suitability of the SFRL for kinetics studies of other molecules was conducted. This study included monitoring the $R\frac{1}{2}(\frac{1}{2})$ transition in NO in a flow system and using a ratio detection scheme with a polarization dependent beam splitter. The conclusion we have reached is that the SFRL is not sufficiently stable in amplitude to conduct kinetics studies (also reached independently by the SFRL group at Heriot-Watt) and that its major roles lie in its absolute frequency measurement capabilities and pollutant identification potential. Further development of the SFRL has been set aside and the SFRL dewar has been modified to accommodate a semi-conducting diode laser. A diode laser (whose frequency will span the 1696 cm^{-1} band of HONO) and a control unit have been purchased, and we expect to take the first high resolution spectra at HONO in the near future. The CO laser operating at 1696.512 cm^{-1} should provide a reference point for the calibration of the spectra.

The production and identification of gaseous nitrous acid (HONO) is of interest due to the expected participation of HONO in the chemistry of both the stratosphere and troposphere. A high quality source of nitrous acid, free of nitric oxide and nitrogen dioxide, is highly desirable both for spectroscopic and kinetic measurements. To this end the reaction of gaseous hydrogen chloride with solid sodium nitrite has been suggested. We have investigated the reaction of HCl with a heated column of potassium nitrite (I) on the NOAA flowing afterglow and are presently trying to make quantitative measurements of HONO production by iodometric procedures.

$$HCl(g) + KNO_2(s) \overset{\Delta}{\rightarrow} HONO(g) + HCl(s) \qquad (I)$$

On the flowing afterglow H_3O^+ was used as a proton donor and an attempt was made to monitor the production of H_2ONO^+. The latter, protonated nitrous acid, was observed, but in very low ratio to NO^+. We ascribe that to the weakness of the HO..NO bond which is broken during the proton transfer reaction. The results do indicate production of HONO, but various tests made on the flowing afterglow with NO and NO_2 could not rule out the possibility that reaction (I) goes partially as:

$$2HCl(g) + 2KNO_2(s) \overset{\Delta}{\rightarrow} NO(g) + NO_2(g) + H_2O(g) + +2KCl(s).$$

The iodometric technique being used to attempt to measure the quantitative production of HONO is to trap the HONO as nitrite ion in neutral or basic solution. The nitrite ion oxidizes I^- to I_3 which is then titrated back to I^- with standardized thiosulfate solution. Preliminary measurements indicate a yield of 60% or better of oxidant from reaction (I), but unfortunately once again HONO cannot yet be distinguished from a mixture of NO and NO_2 (N_2O_3) which is in fact the anhydrous form of HONO. This problem is being pursued further.

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3.10 Microwave Spectroscopy of Atmospheric Contaminants

Project Leader: D. R. Johnson, Optical Physics Division

Other Personnel: R. D. Suenram, NBS-NRC Postdoctoral Fellow 1975-1977.

Objective

Over the course of the past decade, there has been a growing concern about atmospheric contamination. Automobiles and various industrial processes were recognized early in the course of analysis as being major contributors to atmospheric contamination. More recently, the commonly used fluorocarbon refrigerants and aerosol propellants have presented yet another type of atmospheric contamination problem. Direct measurements of the concentrations of these contaminating molecules or their reaction products in the atmosphere have proved to be extremely difficult. However, the importance of these measurements to provide bench marks for theoretical calculations cannot be overstated. For many molecules, ground-based radio astronomical techniques offer a convenient and unambiguous way of getting information on the vertical profile as well as the column abundance. However, before measurements of this type can be made it is essential that the microwave spectrum of the molecule in question be thoroughly studied in the laboratory. It is the objective of this research effort to provide detailed laboratory analysis for atmospheric pollutants that can potentially be observed by astronomical techniques.

Approach

We currently have in operation three independent microwave spectrometers with special facilities for handling short-lived and reactive molecules. Our spectral coverage parallels that of the existing radio telescopes and we have had extensive field experience with a variety of radio telescope systems. Past experience has shown that the molecular transitions that offer the best possibilities for telescope studies are not necessarily the same transitions that are easily studied in the laboratory. Our approach is to analyze the microwave spectrum of the molecule in detail in order to produce a set of molecular parameters of known accuracy. The resultant molecular parameters are then used to make a reliable prediction of the entire microwave spectrum of the molecule. Relative intensities for the various spectral lines can be calculated with reasonable accuracy once the permanent electric dipole moment has been measured.

Progress

Recently it has been suggested that chlorine nitrate could be formed under stratospheric conditions by the 3-body reaction of ClO and NO_2.

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (1)$$

analogous to the OH reaction

$$OH + NO_2 + M \rightarrow HONO_2 + M \qquad (2)$$

Model stratosphere calculations based on these reactions imply that substantial amounts of ClO may be converted to $ClONO_2$. $ClONO_2$ could therefore act as an additional "holding tank" for chlorine and would be expected to decrease the efficiency of chlorine in destroying stratospheric ozone. Since the laboratory microwave spectrum of $ClONO_2$ had not been previously studied, we undertook its investigation.

An existing microwave spectrometer with a new stainless steel and Teflon absorption cell was used for the investigation. The sample was completely contained in stainless steel, Teflon and Pyrex with the exception of one ground glass joint in the inlet system which was lubricated with Kel-F grease. Samples were injected into the absorption cell by allowing $ClONO_2$ to warm up enough to bring the pressure in the system to over 100 μ/Hg. The pressure was then reduced to 20-50 μ/Hg before running by opening the system to the vacuum pump for a few seconds. It should be emphasized that only when the absorption cell was cooled with dry ice and the system free of any small leaks were we able to observe detectable signals from $ClONO_2$ in the gas phase. If the vacuum system was exposed to the atmosphere several injections of $ClONO_2$ were necessary to season the cell before the microwave spectrum could be reproduced.

The microwave spectrum of chlorine nitrate has been observed and analyzed. The molecule was found to be quite prolate ($\kappa = -0.895$) with the dominant electric dipole moment component along the a-principal axis. Hence, the molecule has a "band spectrum" where the most intense transitions follow the selection rule $\Delta J = +1$. The assignment of this particular spectrum to chlorine nitrate was based on several unique spectral characteristics. The observed spectrum is that of a planar molecule with a geometry similar to nitric acid (i.e., Δ = Ic-Ia-Ib is small and positive). The ^{37}Cl form of the molecule was readily identified (1/3 the intensity of ^{35}Cl) and the rotational constants agree well with the expected mass shift (see Table 3.10.1) Many of the observed transitions show splittings characteristic of effects from the nuclear quadrapole moments of a chlorine atom attached to the end of the molecule. All of this information considered together offers strong proof that the molecule under investigation is indeed $ClONO_2$. Stark effect measurements have been carried out on several transitions of $ClONO_2$ leading to $\mu_a = 0.71 \pm .10$ Debye, $\mu_b = 0.22 \pm 0.02$ Debye and $\mu_c = 0$.

During the early stages of these experiments, a new molecular species was observed in the sample cell. At the time the sample appeared to have a slightly higher vapor pressure than it did during the later stages of the experiment. It appears, therefore, that the sample, as it was originally synthesized, contained this second molecular species as a slightly more volatile constituent. Since the new molecule was not anticipated and its microwave spectrum had not been previously studied, it had to be identified from the spectral characteristics alone. The microwave spectrum of the new molecule was characterized by intense, a-type, R-branch bands, which were in many ways similar to those of $ClONO_2$ but shifted somewhat in frequency.

Spectral assignment has now been completed on the main isotopic form with the resulting rotational constants:

$$A = 31578.7 \pm 1.1 \text{ MHz}$$
$$B = 2691.03 \pm 0.03 \text{ MHz}$$
$$C = 2560.89 \pm 0.03 \text{ MHz}$$

The B and C rotational constants are not very different from those of $ClONO_2$ itself but the inertial defect ($\Delta = I_c - I_a - I_b$) is quite large, clearly indicating that the new molecule is non-planar. Thus far, transitions active through dipole moment components along both the a- and b-principal axes have been observed. The moment in the c direction has been shown to be small and may well be negligible. Quantitative measurements of μ_a and μ_b have not yet been made but qualitative comparisons indicate that the moments are about 3 times larger than their respective counterparts in $ClONO_2$. A second spectrum essentially identical in character to the spectrum of the new molecule but with 1/3 the intensity has also been located. Both the intensity and frequencies of the individual lines of the new spectrum are consistent with a molecule containing an isotopic substitution on a single chlorine atom. Splittings of individual lines much like those of $ClONO_2$ have also been found in the spectrum of the new molecule implying that the chlorine atom is in an end position. From the observed set of rotational constants the molecule must contain at least 3 but no more than 4 atoms in addition to the Cl atom. Considering the starting compounds used for the preparation of the initial sample it is clear that these 3 or 4 additional atoms must be formed from some combination of O and N. With all of the evidence in hand we were forced to conclude that the new molecule is ClONO in a non-planar zig-zag structure. ClONO could well have been formed during our initial sample preparation through the reaction,

$$Cl_2O + NO + NO_2 \rightleftarrows 2ClONO \quad (3)$$

which is analogous to the well known reaction

$$H_2O + NO + NO_2 \rightleftarrows 2HONO \quad (4)$$

ClONO may be formed under stratospheric conditions by a 3-body reaction analogous to reaction (1)

$$ClO + NO + M \rightarrow ClONO + M \quad (5)$$

The importance of ClONO in stratospheric models can only be determined when reaction rate and absorption cross section information become available.

Table 3.10.1
Rotational Constants for the Ground and First Vibrational State of Chlorine Nitrate (MHz)

		^{35}Cl	^{37}Cl
v = 0	A	12108. ± 5.0[a]	12108.2 ± 4.2
	B	2776.96 ± 0.05	2700.91 ± 0.04
	C	2258.07 ± 0.04	2207.55 ± 0.04
v = 1	A	12008. ± 6.0	12003.5 ± 6.0
	B	2776.75 ± 0.06	2700.81 ± 0.05
	C	2262.06 ± 0.05	2211.42 ± 0.04

[a] The error limits represent two standard deviations of the fit.

4. Electron Energy Loss Spectroscopy

Project Leader: R. J. Celotta, Optical Physics Division

Objective

To develop electron energy loss spectroscopy as a gas analysis technique and to determine its sensitivity and advantages as applied to particular measurement problems.

Approach

The magnitude of the unique electron energy loss spectrum of a gas or vapor is used to determine its identity and relative concentration within a gas sample. Data is accumulated on a mini-computer, which can, for simple problems, calculate the concentrations, or in complex cases, will prepare the data for analysis on a larger computer.

Progress

The sensitivities for detection of methane, ethane, acetylene, nitrous oxide, trichloroethylene, trichloroethane, freon 12 and freon 22, in oxygen, were determined by fitting low concentration spectra with pure spectra of the constituents.[1] Duplicate measurements and fits were made to estimate the overall reproducibility. The apparatus was improved by a reworking of its detection electronics and changes in the electron beam handling power supplies.
Additional work was performed on determination of oscillator strengths or photo absorbtion cross-sections, for various atmosphere gases and pollutants. Determinations were made for freons 11 and 12[2], oxygen[3], acetone[4], methane[5], n-Hexane[5 and nitrous oxide[6]. The freon results helped resolve a controversy between conflicting optical data.

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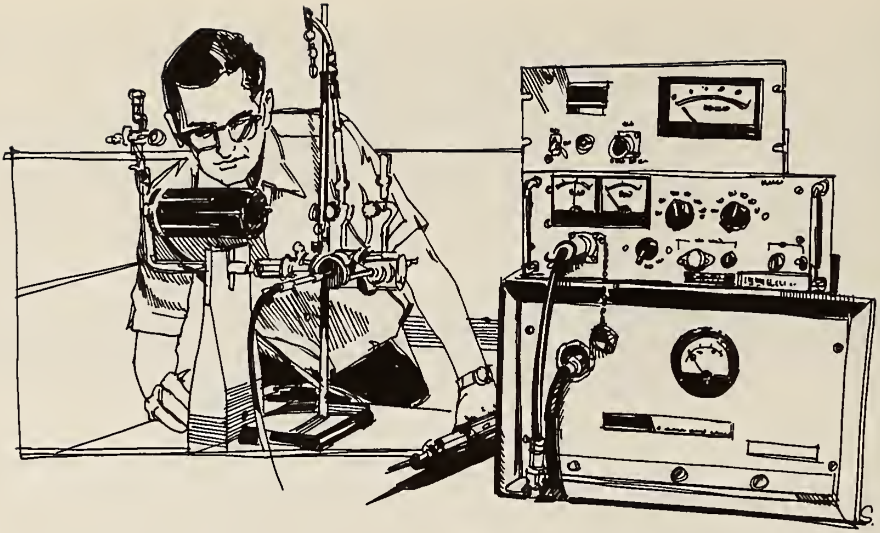

5. Freon Photochemistry

Project Leaders:	P. Ausloos, A. M. Bass, Physical Chemistry Division
Other Personnel:	A. Ledford, R. E. Rebbert

Objective

To determine absorption cross sections and the quantum yields of photolysis of Freon 11 and Freon 12 in the stratospheric window region (195-210 nm), and the photodecomposition of CCl_4, CH_3Cl, $CHFCl_2$ (Freon 21) and CHF_2Cl (Freon 22).

Progress

Since chlorine atoms catalyze the chain decomposition of stratospheric ozone, this project sought to measure quantum yields of the photolyses of the Freons, the major suspected source of stratospheric chlorine atoms, and to determine the modes of decomposition of chlorofluormethanes. An investigation of the photodissociation of $CFCl_3$ (Freon 11) and CF_2Cl_2 (Freon 12) in the presence of a chlorine atom interceptor has been carried out in the important stratospheric window region (195-210 nm). It was found that one Freon molecule dissociates per photon. Depending on the wavelength, decomposition of the Freon molecule may result in the release of one or two chlorine atoms. The shorter the wavelength the greater the probability that two chlorine atoms detach themselves from the photoexcited Freon molecule. It has furthermore been demonstrated that detachment of a Cl_2 molecule or an F atom from Freon 11 and Freon 12 occurs with a very low probability (<0.001).

In order to obtain accurate photodecomposition quantum yields at stratospheric temperatures (200-275K), it will be necessary to measure the absorption cross section of the Freons at the temperature and pressure at which the photolysis experiments are to be carried out. Preliminary measurements carried out by us at 213.9 nm have shown that the absorption cross section of Freon 12 decreases sharply at temperatures below 300 K. It follows that values reported in the literature, which are invariably measured at room temperature (unspecified), cannot be used to determine photodissociation quantum yields with a high degree of accuracy.

As a follow-up of the investigation of the photodissociation of $CFCl_3$ and CF_2Cl_2, the CCl_4 photolysis has been elucidated. Contrary to recent reports in the literature, absorption of a photon by CCl_4 does not lead to the elimination of a chlorine molecule. Instead, at the long wavelength end of the solar spectrum a chlorine atom is detached with a quantum yield equal to unity. As was observed in the case of $CFCl_3$ and CF_2Cl_2, the shorter the wavelength the greater the probability that two chlorine atoms detach themselves from photoexcited CCl_4.

These photochemical investigations will be extended to establish the photodissociative channel (S) of CH_3Cl, which has been shown to be a major natural source of chlorine in the stratosphere. In addition, the photodecomposition of possible chlorofluorocarbon substitutes HCF_2Cl and $HCFCl_2$ will be investigated. Preliminary experiments carried in this laboratory have shown that photoexcited HCF_2Cl splits out HCl rather than a chlorine atom. If this judging is corroborated by further experimentation, it would indicate that photodissociation of HCF_2Cl would have relatively little effect on the ozone layer.

6. Chlorine-Atom Kinetics

Project Leader: Michael J. Kurylo, Physical Chemistry Div.
Other Personnel: Ronald G. Manning and Walter Braun

Objective

The recent inquiry into the possible role that naturally occurring or man-made chlorine containing compounds might play in determining the chemistry of the earth's stratosphere has resulted in an upsurge of interest in chlorine atom gas phase reactions. Interruption of the Cl-ClO chain can occur *via* the reaction

$$\mathrm{Cl} + \mathrm{RH} \rightarrow \mathrm{HCl} + \mathrm{R}$$

whereby Cl is converted into less reactive HCl. The most logical candidates for reactants (RH) are CH_4 (abundant at midstratospheric levels with a mixing ratio (v/v) of 10^{-6}) and CH_3Cl (10^{-19} mixing ratio).

Until recently, however, the only direct reaction rate data for Cl atoms with either of these species were obtained for temperatures at or above 288K. Unlike the reactions of O atoms with CH_4 and CH_3Cl, the Cl reactions were observed to have vastly different Arrhenius A factors and equal activation energies. A very recent study of Cl + CH_4 from 218-401 K is in reasonable agreement with the two earlier studies at 288 K but differs significantly from the values predicted by the only other temperature dependent study.[1-4]

Approach

For these reasons we have undertaken a systematic study of H atom metathesis by Cl atoms for the following reactions:

$$\mathrm{Cl} + \mathrm{CH_4} \xrightarrow{k_1} \mathrm{HCl} + \mathrm{CH_3}$$

$$\mathrm{Cl} + \mathrm{CH_3Cl} \xrightarrow{k_2} \mathrm{HCl} + \mathrm{CH_2Cl}$$

$$\mathrm{Cl} + \mathrm{CH_3F} \xrightarrow{k_3} \mathrm{HCl} + \mathrm{CH_2F}$$

$$\mathrm{Cl} + \mathrm{C_2H_6} \xrightarrow{k_4} \mathrm{HCl} + \mathrm{C_2H_5}$$

Standard flash photolysis resonance fluorescence techniques were used to obtain rate expressions in units of cm^3 $molecule^{-1}s^{-1}$.

$k_1(218\text{-}322K) = (7.83 \pm 1.53) \times 10^{-12}\exp[-(2528 \pm 101)/RT]$

$k_2(233\text{-}322K) = (3.36 \pm 0.71) \times 10^{-11}\exp[-(2484 \pm 113)/RT]$

$k_3(216\text{-}286K) = (4.79 \pm 1.05) \times 10^{-12}\exp[-(1595 \pm 107)/RT]$

$k_4(222\text{-}322K) = (7.29 \pm 1.23) \times 10^{-11}\exp[-(121 \pm 87)/RT]$

The results are in good agreement with subsequent resonance fluorescence studies but conflict with high temperature (>300K) discharge flow mass spectrometric values obtained for CH_4 and CH_3Cl reactants. The discrepancies are due to either systematic errors in one or both of the techniques or to curvature in the Arrhenius type temperature plots. A full range (200-1000K) temperature study is needed to resolve this difference.

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7. The Fluorescence Detection of Nitric Oxide

Project Leader: Hideo Okabe, Physical Chemistry Division
Other Personnel: Frederick P. Schwarz

Objective

Development of a simple, rapid and highly accurate fluorescence technique to measure the NO concentration in standard reference mixtures of NO in N_2. Investigate the potential application of this method for measuring NO in automotive exhaust gas and in air.

Approach

An approach has been adopted based on experience with the development of the ambient (ppb) SO_2 in air fluorescence monitor[1]. The NO absorption begins around 230 nm and proceeds down into the vacuum ultraviolet. The emission from the $A^2\Sigma^+$ state of NO excited by the zinc resonance line at 213.86 nm extends from the resonance line to 310.0 nm and has a maximum around 260 nm[1]. At concentrations in the ppm range, the fluorescence should be linearly proportional to the concentration if the 213.86 nm line intensity is constant and if no self quenching takes place. However, the quenching of the $NO(A^2\Sigma^+)$ by NO and gases other than N_2 is fairly efficient. In the case of NO in N_2, the fluorescence intensity would become sublinear with respect to the concentration at high NO concentrations.

Progress

The quenching of the NO fluorescence in N_2 by the presence of third gases was investigated. The gases chosen were H_2O vapor, CO, CO_2, C_2H_4, C_3H_8, and O_2, all of which are present in automobile gas emissions.[2]

Four runs consisting of 57 measurements of NO in N_2 at concentrations from 250 ppm to 0.0153 ppm were performed in a static sampling system. The static sampling system consisted of the fluorescence cell connected to a vacuum system and a large mixing vessel. An initial mixture of 250 ppm NO in N_2 was diluted successively by N_2 in the mixing vessel and a sample of each mixture was introduced into the evacuated cell and its fluorescence measured. Least squares fits of the signal, F, to the following equation were calculated.

$$F = A [NO] - BF [NO] + F_o$$

F_o is due to the scattered light from the 213.86 nm radiation and the fluorescence of NO impurity present in the N_2 diluent gas. B is a constant mainly due to the fluorescence self quenching of NO. From the values of A, B, and F, determined in each run, the NO concentrations were recalculated from the signal measurements. Over 50% of the 57 calculated concentrations were within 3% of the actual concentrations.

Five different primary standards of NO in N_2 were diluted by a calibrated mass flowmeter and the NO fluorescence measured. The sampling was done in a flow system where the samples at flow rates of ~10ℓ/min were continually passed through the fluorescence cell which was open to the atmosphere. The concentrations, signals, and calculated concentrations are presented in Table 7.1. An error of 1.0% in the concentrations yielded a residual standard deviation of 0.468. The deviation between the actual and calculated values is less than 1.2%. The technique can be applied to concentrations as high as 932 ppm.

The quenching constants of NO fluorescence by various automotive exhaust gases are given in Table 7-2.

Concentrations, signals, and calculated
Concentrations of standards of NO in N_2

Table 7.1.

Initial Mixture of NO in N_2	Prepared Conc. (ppm)	Photon Counts	Cal. Conc. (ppm)
5136 ppm	20.4	93,424 ± 446	20.3
1067 ppm	18.6	87,063 ± 743	18.6
1.917%	118	428,307 ± 1323	117
0.9913%	122	441,267 ± 447	121
1.515%	123	448,737 ± 1429	123
"	261	823,400 ± 3872	258
"	239	778,520 ± 2571	240
"	932	1,896,227 ±10,761	924
"	316	961,990 ± 2362	317
"	193	652,854 ± 2093	193

Parameters	Standard Dev.
$A = 1.03 \times 10^{-3}$ ppm^{-1}	1.13%
$B = 3964$	0.431%
$F_o = 14,722$	6.73%

Table 7.2

Quenching Constants of NO fluorescence by some Automotive Exhaust Gases

NO Fluorescence-Quenching Gas	Approximate Composition Range in % Vol. of Auto. Exhaust Gas	Quenching Constant B in Torr^{-1} after Dilution of Sample by 100 to 1 with N_2	% Fluctuation of C_{NO} after Dilution by 100 to 1 with N_2 at 760 Torr and at 24°C
H_2O	13.0 to 13.2	0.90	47 to 47
CO	0.8 to 5.2	0.07 ± .01	0 to 3
CO_2	9.5 to 10.2	0.90	39 to 41
O_2	~0	0.50	0
C_2H_4	0 to 0.2	0.10	0 to .15
C_3H_8	0 to 0.2	0.01	~0
H_2	0.2 to 1.7	0.005	~0
	Total Variation of the C_{NO}		0 to 5
	Total Variation without CO_2		0 to 3

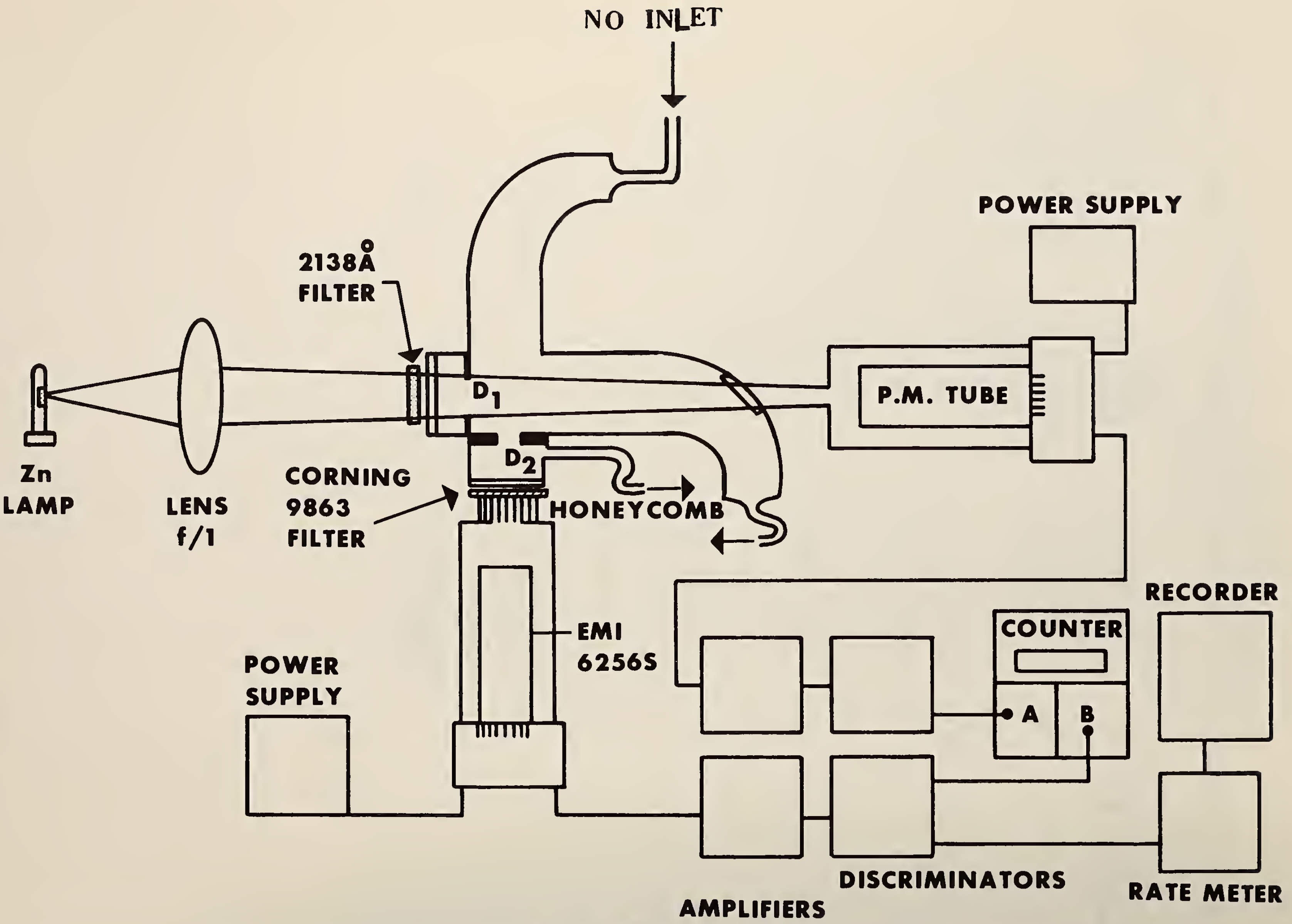

Figure 7.1 The apparatus for the measurement of quenching of NO fluorescence by various gases

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8. Effect of Polymeric Structure on Permeation Tube Uniformity

Project Leader: D. H. Reneker, Polymers Division
Other Personnel: G. M. Martin, J. D. Barnes

Objective

To identify the sources of variability in the permeation rate of permeation tubes so that appropriate measures can be taken to obtain uniform tubing and minimize the cost of SRM permeation tubes. Presently, each permeation tube is individually calibrated although ideally, only randomly selected tubes should be calibrated in certifying a lot.

Approach

Observe and describe the morphology of the polymer in the tube. Identify the morphological variables that have the greatest effect on permeation rate. Communicate results to manufacturers of the tubing used in permeation tubes so that highly uniform batches of tubing can be obtained.

Progress

In work reported previously[1] an excellent negative correlation of permeation rate with the density of the tube walls was established for SO_2 permeation tubes made from a fluorocarbon copolymer. The least squares line fitted to the data had the equation $P = 102.95 - 46.90\rho$ with a residual deviation of 0.02/μg/min where P is permeation rate in μg/min and ρ is density in g/cm^3. The factors that make the density vary include essentially all the geometrical features that cause the polymer molecules to depart from a perfect crystal structure, such as crystallographic defects, disorder around chain ends or side branches, disorder in the interlamellar regions and microvoids. The measured density is an average of the effects of all such defects that are present in the sample.

The permeation rate also depends on these same geometrical features, but in an independent way. For example, suitably connected defect arrays can provide effectively shorter pathways for the permeation molecule. Unfavorably oriented, defect free lamellae can act as barriers that greatly reduce the permeation rate since permeation through lamellae is slower than between them. Neither the way the defects are connected nor the orientation of the lamellae would necessarily affect the density. Therefore we looked beyond the density into the morphological details of the sample in order to identify more fundamental factors which can cause variations in the permeation rate. The dominant morphological feature of this fluorocarbon copolymer is its tendency to form stacks of folded chain lamellar crystals a few tens of nanometers thick. Most of our effort was concentrated upon the characterization of this lamellar morphology using techniques such as X-ray diffraction, optical microscopy, and electron microscopy.

The morphological features that were actually observed in the walls of these permeation tubes are summarized in Fig. 8.1 which is a schematic diagram of a longitudinal section of the tube wall. The size (S) of the polyhedral stacks of lamellae is roughly to scale although the stacks are not as perfect as indicated. The stacks may be thought of as parts of spherulites, although the spherical morphology is not well developed in these extruded tubes. The dark lines represent the nearly planar boundary regions between the stacks of lamellae. The thickness of the lamellae (L) is greatly exaggerated in the diagram. The angle ϕ is the angle between the normal to a stack of lamellae ($\vec{n}$) and the radial direction ($\vec{r}$). The parameters S, L, and ϕ which characterize each stack of lamellae are all functions of radial position ($\vec{r}$). An X-ray beam with a diameter of 200 μm permitted diffraction patterns to be obtained from regions at radial positions near the outer surface, the middle, and the inner surface of the tube wall, as indicated in Fig. 8.2.

The relation between the lamellar thickness (L) values at different radial positions and the permeation rate are shown in Fig. 8.3. The lamellar thickness increased from about 26 nm near the outer surface to about 33 nm near the inner surface. There was also a definite tendency for tubes with higher permeation rates to have thicker lamellae at all three radial positions.

An experimental orientation index (η) related to the local average value of ϕ was derived from optical density scans of the small angle X-ray patterns as shown in Figure 8.2. The value of η was taken as the intensity (E) of X-rays from the lamellae that diffracted in the axial direction divided by the intensity (D) from the lamellae that diffracted in the radial direction. Thus a high value of η means that the stacks of lamellae had their normals more nearly parallel to the tube axis, that is ϕ near 90°. The relation between the orientation index (η) values at different radial positions and the permeation rate is shown in Fig. 8.4.

A theoretical model [2] was developed for permeation through tube walls with the morphological features shown in figure 8.1 Permeation was assumed to occur by different mechanisms in the regions between lamellae and in the regions between stacks of lamellae. This model provides a basis for identification of the parameters which affect the permeation rate and for estimation of the effect of variation of each parameter on the permeation rate.

Our efforts on the characterization of the morphological structure of permeation tubes were described in an invited talk attended by technical representatives or resin producers and extruders at a meeting of the Society of Plastics Engineers in May 1974. An article [2] based on that talk was submitted for publication. Visits were made to Metronics Associates who manufacture the SRM SO_2 permeation tubes and to Dohrmann Associates who manufacture an instrument for measurement of permeation. Contacts were made through IAT with people at NIOSH and OSHA who are concerned with the use of permeation tubes as calibrated dispensers of other gases such as vinyl chloride.

During FY 75 our efforts have been directed toward obtaining or preparing samples with wider ranges of morphological parameters and establishing a facility for measuring permeation rates of such samples.

We designed and purchased components for a permeation measuring facility based on a sensitive gas chromatograph. The gas chromatograph serves as a means of monitoring the concentration of permeant gas in a stream of helium carrier which continuously sweeps the outlet side of a membrane or tube made from the polymer under test. A valving manifold admits pure carrier gas, pure permeant gas, or a controlled mixture of carrier and permeant gas to the inlet side of the polymer sample. The cell containing the sample is thermostatted in a controlled temperature bath. This equipment is designed to permit time-lag-measurements [3], sorption and desorption measurements, and steady state permeation rate measurements.

Experiments were undertaken in which the density of commercially available fluorocarbon tubing was modified by thermal treatment. The density of the fluorocarbon was found to increase to a value higher than any found previously in our studies when a length of tubing was annealed at a temperature just below its melting point.

Melting a length of tubing and then quenching it in ice water yielded no significant change in density. This result agrees with our assessment that the tubing used in manufacturing permeation tubes is a highly quenched material. Procedures were investigated for fabricating samples from the melt for permeation measurements but more reproducible methods are needed.

Contacts with the supplier of SRM SO_2 permeation tubes to NBS revealed that this manufacturer had been unable to get his suppliers to agree to provide fluorocarbon tubing which fell within certain dimensional tolerances. He therefore offered no hope of being able to obtain tubing with a specified density. At the present time, the permeation tube manufacturer makes quality control measurements (length, mass, diameter, etc.) on as-received tubing and is able to estimate whether permeation tubes produced from such tubing will be uniform enough for his purposes. This produces tubes of the right general rate, but it does necessitate individual calibration of SRM tubes and might mask other perturbing effects.

Given that SO_2 permeation tubes must be manufactured at fairly frequent intervals because they cannot be stored for a long time period, it might be desirable for NBS to sequester a supply of fluorocarbon tubing to be furnished to manufacturers of permeation tubes as they need it to make SO_2 and other permeation tubes for NBS. This would be expected to reduce the batch-to-batch variations in permeation rate to the much lower level of the variation observed within a good batch, thereby permitting NBS to supply the measurement system with a less variable product.

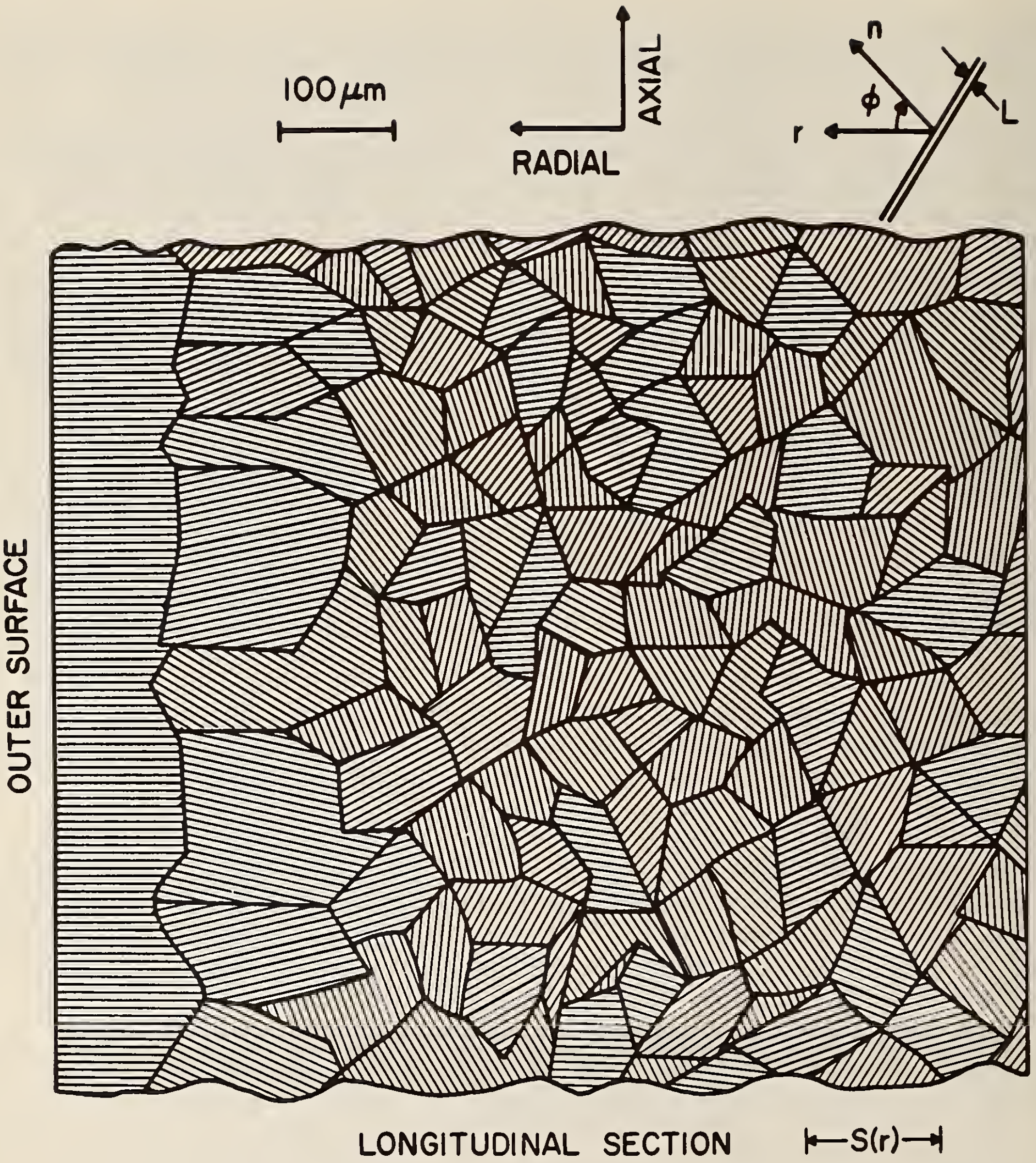

Figure 8.1 - A schematic diagram of the structure in a longitudinal section of the wall of a fluorocarbon copolymer tube.

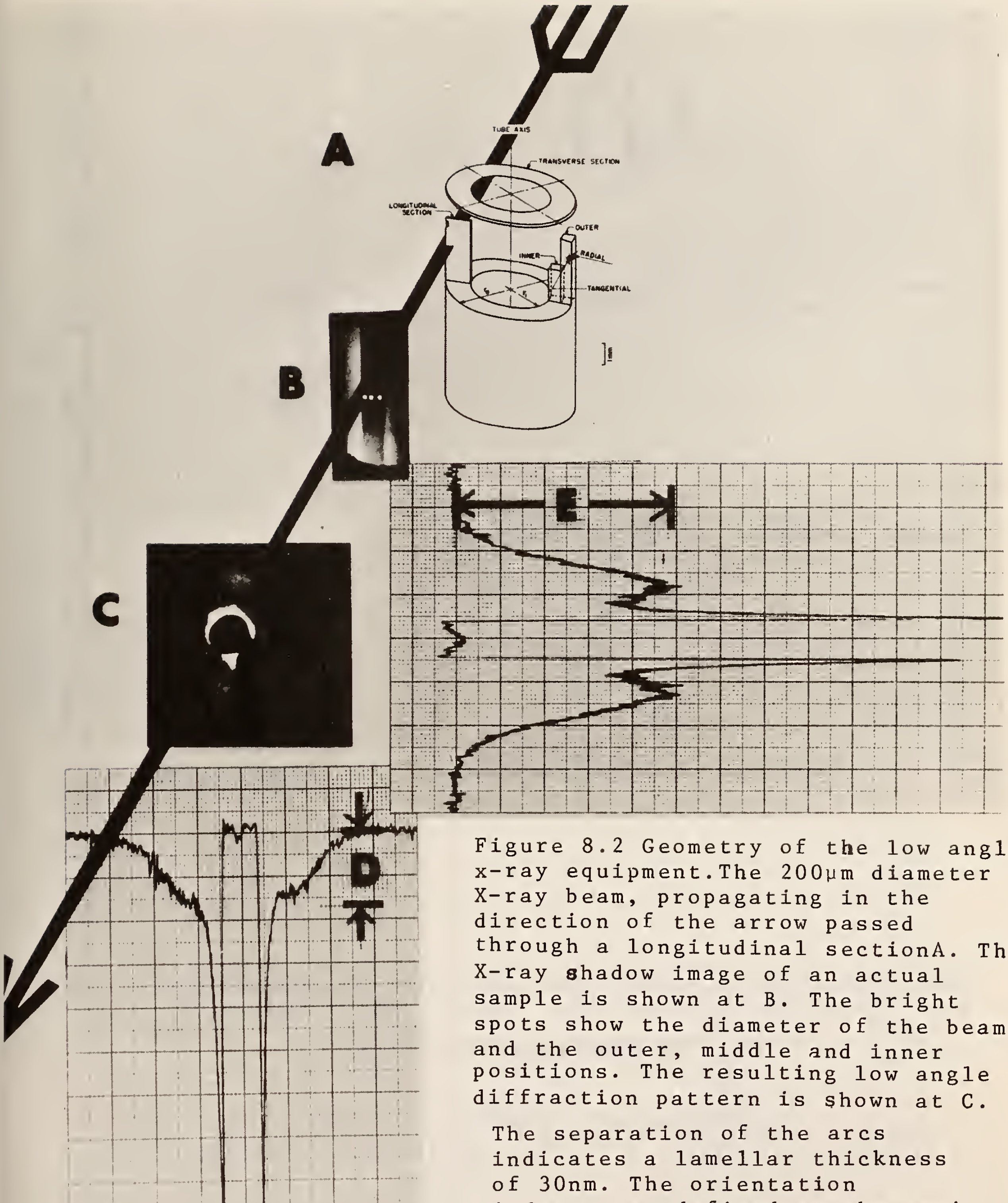

Figure 8.2 Geometry of the low angle x-ray equipment.The 200μm diameter X-ray beam, propagating in the direction of the arrow passed through a longitudinal sectionA. The X-ray shadow image of an actual sample is shown at B. The bright spots show the diameter of the beam and the outer, middle and inner positions. The resulting low angle diffraction pattern is shown at C.

The separation of the arcs indicates a lamellar thickness of 30nm. The orientation index η was defined as the ratio of the distance E shown on the axial optical density trace of the diffraction pattern to the distance D shown on the radial trace.

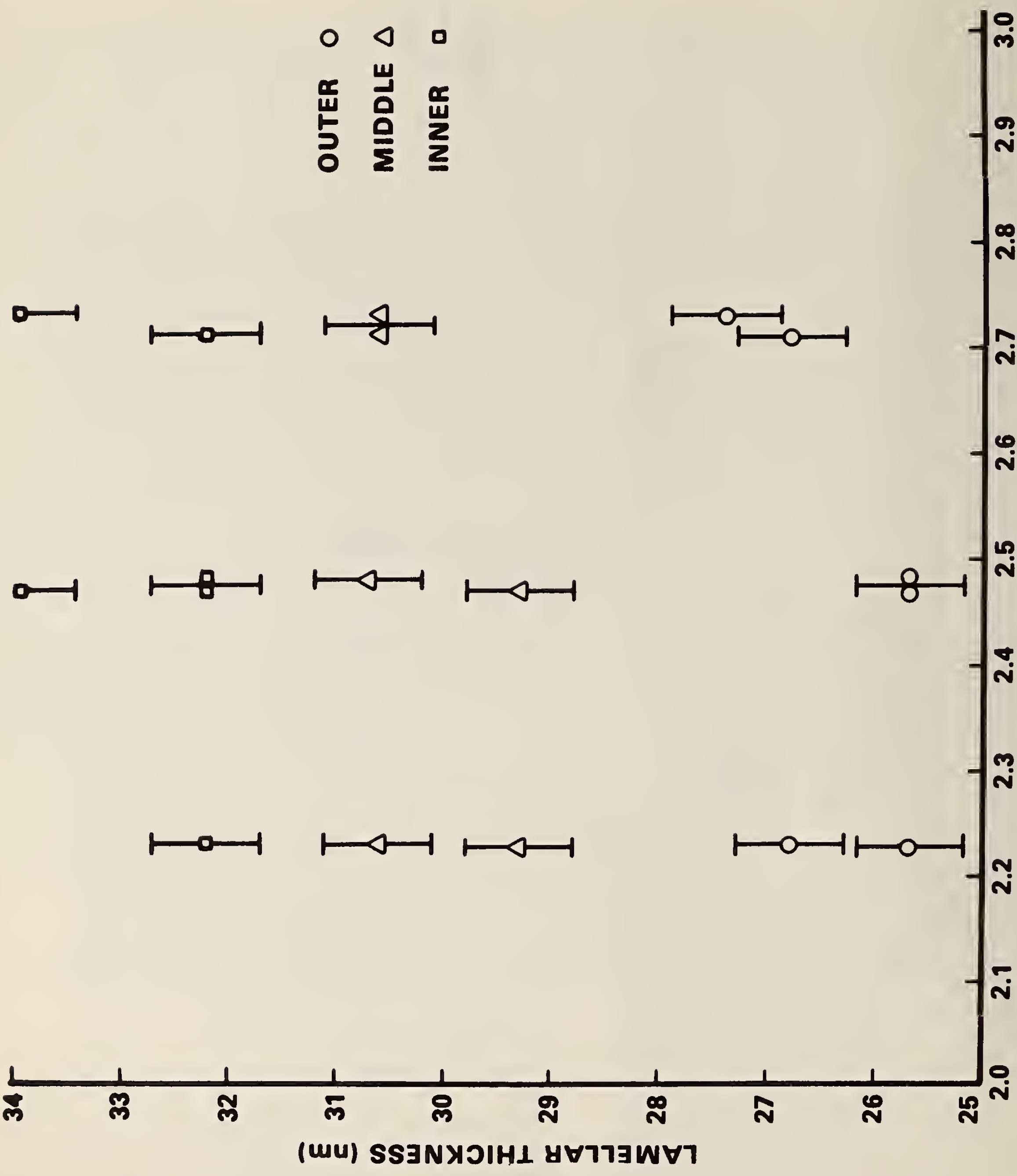

Figure 8 .3 - Relationship between permeation rate and lamellar thickness at various positions in the tube wall.

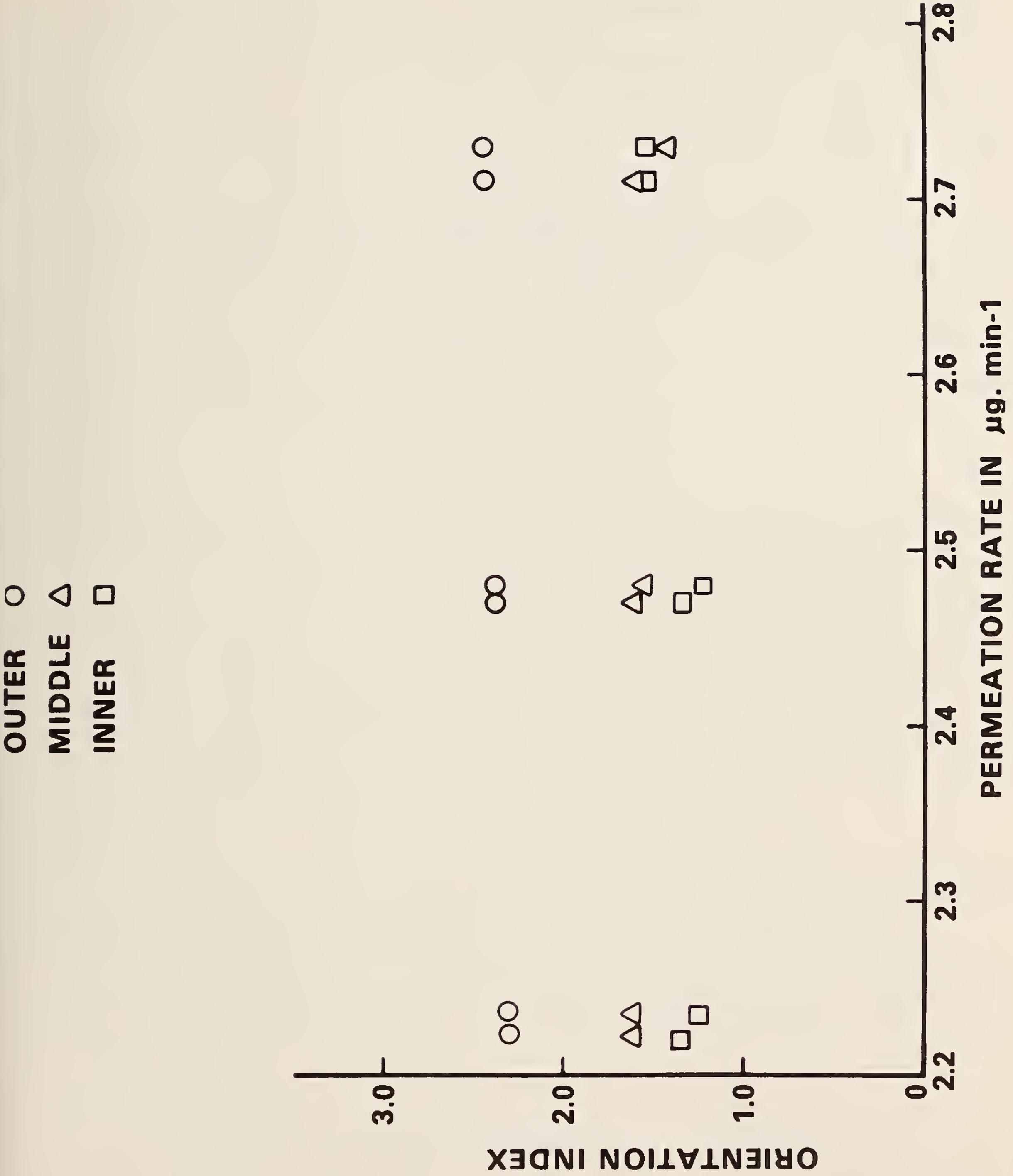

Figure 8.4 - Relationship between permeation rate and orientation index at various positions in the tube wall.

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9. Analysis of Mathematical Models of Integrating Monitoring Devices

Project Leader: R. J. Rubin, Polymers Division

Objective

To provide an analysis of mathematical models for the diffusion of criteria air pollutants (e.g., O_3, SO_2, NO_2, CO) from a turbulent atmosphere to and through a permeable membrane to a reactive substrate. Such analyses show how the barrier--reactive substrate system acts as a device for averaging pollutant concentrations during a period of 24 hours, 1 week, or longer. The analyses also show how material properties, such as gas solubilities and diffusion coefficients, affect the operation of the device.

Approach

Two models of an integrating monitoring device are considered. In the first model (Model I), a permeable membrane backed by a reactive substrate, the transport of gas through the membrane is assumed to be governed by the simple one-dimensional diffusion equation. In a second model (Model II), also analyzed in terms of a one-dimensional diffusion equation, reactive sites which act as traps for diffusing gas molecules are assumed to be uniformly distributed throughout the membrane. In contrast to the case of Model I for which the diffusion equation is linear, the diffusion equation describing Model II is in general nonlinear.

Progress

The simplest version of each of the two model monitoring devices has been analyzed thoroughly. In the case of Model I, a permeable membrane of thickness ℓ which is exposed to the atmosphere is backed by a reactive substrate. The quantity of diffusing pollutant gas immobilized per unit area by reacting with the substrate backing in the time interval T is given by the expression

$$\Phi_I(T) = DS\ell^{-1}\int_0^T p(t)\,dt, \qquad T \gg \tau_R$$

or

$$\Phi_I(T) = Q\ell^{-1}\bar{p}\,T, \qquad T \gg \tau_R \qquad (1)$$

where $Q = DS$ is the permeability of the membrane,

D is the diffusion coefficient of the gas in the membrane,
S is the solubility coefficient (Henry's Law constant) of the gas in the membrane,
ℓ is the polymer membrane thickness,
$p(t)$ is the ambient partial pressure of the pollutant gas as a function of the time, t
$\bar{p}$ is the average ambient partial pressure of the pollutant gas in the time interval T
$\tau_R = \ell^2/D\pi^2$ is the relaxation time to establish a steady-state gradient of gas in the membrane.

For operating times T which are large compared to the relaxation time, τ_R, Model I is a perfect integrator in the sense that the total amount of gas which is immobilized per unit area in the operating time interval T is proportional to the time integral of the partial pressure of the pollutant gas in that time interval.

In the case of Model II, a permeable membrane which is exposed to the atmosphere contains a uniform distribution of trapping sites. The quantity of diffusing gas immobilized in trapping sites per unit area in the time interval T is given by the expression

$$\Phi_{II}(T) = \left[2DSn_0 \int_0^T p(t)\,dt\right]^{1/2}$$

or

$$\Phi_{II}(T) = \left[2Qn_0 \bar{p} T\right]^{1/2} \qquad (2)$$

where n_0 is the initial concentration of trapping sites in the membrane and where the other quantities have been defined following Eq. (1). In the case of Model II, the amount of pollutant gas trapped per unit area of the membrane in the time interval T is proportional to the square root of the time integral of the partial pressure of the pollutant in that interval.

Results and Discussion

The units of $\Phi_I(T)$ and $\Phi_{II}(T)$ for Models I and II can be expressed in moles of pollutant gas collected, or immobilized, per square centimeter of membrane area in the operating time interval T. In order to compare the collecting characteristics of monitor Models I and II, we suppose that each monitor is exposed for 24 hours to an average partial pressure of a pollutant equal to 5×10^{-8} atmospheres. This partial pressure corresponds to the maximum allowable exposure to several criteria air pollutants, namely, 50 ppb. The quantities of gas collected by the two models under the foregoing identical exposure conditions are denoted by $\hat{\Phi}_I$ and $\hat{\Phi}_{II}$. The expressions for $\hat{\Phi}_I$ and $\hat{\Phi}_{II}$ are:

$$\hat{\Phi}_I = 1.47\, Q\ell^{-1} \times 10^{-5} \quad \text{moles cm}^{-2}$$

and

$$\hat{\Phi}_{II} = 5.41\, (Qn_o)^{1/2} \times 10^{-3} \quad \text{moles cm}^{-2}$$

when Q, the permeability, is expressed in the units cm^3 of diffusing gas at S.T.P., cm (membrane thickness) per second per cm^2 (membrane area) per cm of Hg pressure difference across the membrane, where ℓ is the membrane thickness in cm, and n_o is the concentration of trapping sites in moles cm^{-3}.

Typical values of Q lie in the range [1] 10^{-10} to 10^{-8} so values of $\hat{\Phi}_I$ and $\hat{\Phi}_{II}$ lie in the range

$$1.47\,\ell^{-1} \times 10^{-15} < \hat{\Phi}_I < 1.47\,\ell^{-1} \times 10^{-13}$$

and

$$5.41\, n_o^{1/2} \times 10^{-8} < \hat{\Phi}_{II} < 5.41\, n_o^{1/2} \times 10^{-7}.$$

The largest value of n_o which might be achieved is $n_o = 10^{-3}$ moles cm^{-3} and the smallest value of ℓ which might be used is 10^{-2} cm. The optimum estimated ranges for $\hat{\Phi}_I$ and $\hat{\Phi}_{II}$ are then

$$1.47 \times 10^{-13} < \hat{\Phi}_I < 1.47 \times 10^{-11} \quad \text{moles cm}^{-2}$$

and

$$1.71 \times 10^{-9} < \hat{\Phi}_{II} < 1.71 \times 10^{-8} \quad \text{moles cm}^{-2}.$$

Thus Model II appears to be a better collector than Model I. At the same time, it should be pointed out that the most optimistic estimate of the quantity of gas collected in a 24-hour period for the maximum allowable exposure is nevertheless very small.

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10. Atmospheric Chemical Kinetics

Project Leader: John T. Herron, Physical Chemistry Division
Other Personnel: Robert Huie

Objective

The general objectives of this program are the quantitative understanding of the chemical processes whereby primary pollutants are formed and subsequently transformed into the noxious compounds typical of polluted urban atmospheres.

Specific goals over the next 2 to 3 years are:

a) Understanding the atmospheric reactions of ozone with the olefins

b) Understanding the atmospheric oxidation of SO_2

c) Understanding the atmospheric oxidation of organic sulfides

Approach

These goals encompass a wide range of chemical species and a large number of chemical reactions, some of which are probably yet to be identified.

Ideally, the experimental approach should involve both the study of elementary reactions, and phenomenological studies of complex systems. An essential compenent of this type of approach is a capability for the mathematical modelling of these systems.

Mathematical and computer capabilities have reached a stage of development such that real processes and real systems are now beginning to be quantitatively described in terms of real chemical (and physical) processes. The model is increasingly the central element in understanding air pollution chemistry, and is a major driving force in planning experimental programs.

To contribute towards the goals outlined in the first section, the following approach is proposed:

A. Phenomenological Studies

1. Stopped-flow Mass Spectrometry. This technique permits the measurement at low pressure (2 to 15 torr), in real time, of the rates of change of reactants and products of chemical reactions. Reaction rate constants

and mechanisms may be deduced from these kinds of experiments. Particular systems to be studied include:

a) Ozone-olefin reactions

b) Oxidation of SO_2 in ozone-olefin mixtures

c) Ozone-sulfide reactions

2. Atmospheric Chemistry Simulation. This involves studies under real atmospheric conditions of subunits of air pollution chemistry. For example, the system O_3, C_3H_6, SO_2; or the system NO, NO_2, C_3H_6, SO_2, $h\nu$ (u.v.). The analytical approach to this type of work has not been chosen. The possibilities include long path infrared, laser Raman, mass spectrometry, gas chromatography, or combinations of these and other approaches. Modelling is an essential element.

B. Elementary Reaction Studies

1. Flow-tube Mass Spectrometry. This involves the formation and reaction of free radicals under steady-state conditions. Amongst the great many reactions of interest the following are given as examples:

a) $HCO + O_3 \rightarrow HCO_2 \xrightarrow{CH_2O} HCOOH$

b) $RO_2 + SO_2 \rightarrow RO + SO_3$

c) $CH_3 + O_3 \rightarrow CH_2O + H + O_2$

d) $O_3 + C_4H_8 \rightarrow$ radicals, stable products

2. Crossed Beam Mass Spectrometry. This involves crossing two intense beams of reacting gases with detection of reaction products by means of mass spectrometry. Some possible reactions to be studied are:

a) $SO_2 + CH_3$

b) $O_3 + CH_3$

This approach is limited to fast reactions for which $k \geq 10^{-2}$ collision rate.

3. Flash Photolysis-Resonance Fluorescence. This is an approach which hopefully can be made available when highly accurate rate measurements on simple species such as H, O, and OH are required.

C. Modelling

The modelling component of this program will be restricted to the modelling of small scale simulation experiments. Existing NBS modelling capabilities developed for the NBS fire program, will be modified and expanded for use in atmospheric chemistry simulation. Ideally, this capability will be made available through time-share computer facilities using laboratory sited computer terminals.

A comprehensive study of significant reactions in the atmospheric chemistry of ozone has been initiated. The initial part of this work has been concerned with the rates of reaction of ozone with atmospheric pollutants. The reaction $O_3 + NO_2 \rightarrow NO_3 + O_2$ has been studied[1] from 259 to 362K, and the rate constant found to be $k = 9.44 \pm 2.46 \times 10^{10} \exp(-2509 \pm 76/T)$ cm $mol^{-1}s^{-1}$.

The major experimental effort has been devoted to studies of ozone-olefin reactions using a stopped-flow reactor with photoionization mass spectrometer detection.[2,3] Product yields have been measured in real time for $O_3 + C_2H_4$, C_3H_6, iso-C_4H_8, and cis-2-C_4H_8.

It was found that rate constants for the reactions of ozone with olefins in the presence of a large excess of molecular oxygen were considerably smaller than those measured in the absence of molecular oxygen. This effect was attributed to the scavenging of free radicals by oxygen, resulting in elimination of chain decomposition of ozone.

Rate constants, measured in the presence of molecular oxygen are as follows (in units of $cm^3\ mol^{-1}s^{-1}$):

$$\log k\ (\text{1-butene}) = (9.247 \pm 0.033) - (1686 \pm 20)/2.303T$$

$$\log k\ (\text{2-methylpropene}) = (9.281 \pm 0.026) - (1671 \pm 23)/2.303T$$

$$\log k\ (\text{cis-2-butene}) = (9.272 \pm 0.087) - (956 \pm 54)/2.303T$$

$$\log k\ (\text{trans-2-butene}) = (9.555 \pm 0.069) - (1051 \pm 43)/2.303T$$

$$\log k\ (\text{2-methyl-2-butene}) = (9.582 \pm 0.119) - (826 \pm 78)/2.303T$$

$$\log k\ (\text{2,3-dimethyl-2-butene}) = (9.230 \pm 0.237) - (294 \pm 196)/2.303T$$

A good linear correlation was found between the activation energy for the reaction and the ionization potential of the olefin. The mechanisms of the ozone-olefin reactions were studied using a stopped flow reactor with photoionization mass spectrometer detection. Product yields have been measured in real time for $O_3 + C_2H_4 + C_3H_6$, 180-C_4H_8 and cis 2-C_4H_8.

The reactions are complicated by free radical chains involving OH, HO_2, CHO, RO, and RO_2. The primary products are probably an aldehyde (or ketone) and a biradical intermediate (the Criegee intermediate or zwitterion).

$$O_3 + \text{olefin} \rightarrow RCHO + RHCOO$$

The decomposition or reaction of the biradical leads to the formation of free radicals. For the ethylene reaction the postulated mechanism under conditions $O_3 > C_2H_4$ is:

$$O_3 + C_2H_4 \rightarrow CH_2O + H_2COO$$

$$H_2COO \rightarrow H_2 + CO_2$$

$$\rightarrow 2H + CO_2$$

$$\rightarrow H + HCO$$

$$H + O_3 \rightarrow OH + O_2$$

$$OH + C_2H_4 \rightarrow \text{Products}$$

$$OH + CH_2O \rightarrow H_2O + HCO$$

$$HCO + O_2 \rightarrow HO_2 + CO$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$HCO + O_3 \rightarrow HCO_2 + O_2 \quad H + CO_2 + O_2$$

Computer modelling of this system using a more complete reaction scheme has been carried out using the computer program of R. L. Brown. The existing photoionization mass spectrometer uses an argon resonance lamp with photon energies no greater than 11.8 eV. This is not enough to ionize and detect CO, CO_2, O_3, or H_2O. It is hoped that use of a neon resonance lamp (energy, no greater than 16.8 eV) will allow these products to be detected.

A critical question which needs to be answered in these studies, in whether or not species such as the biradical intermediate have long lifetimes and hence can qualify as SO_2 oxidizers.

In addition to studying the ozone-olefin system, rate constants were measured for a set of halo-olefins as a contribution to the stratospheric chemistry program. The rate constants, at room temperature are:

$$k(C_2H_3Cl) = 2.2 \times 10^5 \ cm^3 \ mol^{-1}s^{-1}$$

$$k(C_2H_3F) = 2.4 \times 10^5 \ cm^3 \ mol^{-1}s^{-1}$$

$$k(1,2\text{-}C_2H_2Cl_2) = 1.4 \times 10^5 \ cm^3 \ mol^{-1}s^{-1}$$

$$k(1,2\text{-}C_2H_2F_2) = 3.9 \times 10^5 \ cm^3 \ mol^{-1}s^{-1}$$

For comparison,

$$k(C_2H_4) = 1.0 \times 10^6 \ cm^3 \ mol^{-1}s^{-1}$$

The rate constants reported here are about a factor of 5 greater than had been previously reported on the basis of relative rate measurements carried out in solution.

Studies of the reaction of ozone with organic sulfides have also been initiated. These reactions appear to be very fast but the dependece of rate on concentrations suggests that the reaction is predominately a free radical chain process in which the OH radical may play a dominant role.

Some preliminary studies have been made on the reactions of ozone with organic sulfides. The reactions are surprisingly fast (comparable to $O_3 + C_2H_4$) and indicate a possible mechanism:

$$O_3 + R\text{-}S\text{-}R \rightarrow (R)_2SO^* + O_2$$

$$(R)_2SO^* \rightarrow RSO + R \quad \cdot$$

$$R + O_3 \rightarrow \text{aldehydes, etc.}$$

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[a] Supported in part by the Office of Air and Water Measurement.

11. Climatic Assessment Program

Project Leaders: David Garvin and Robert F. Hampson

Other Personnel: J. T. Herron, R. L. Brown, R. E. Huie,
J. D. McKinley, W. Tsang, W. Braun,
M. J. Kurylo, A. H. Laufer, H. Okabe,
L. H. Gevantman, M. D. Scheer

Objective

To evaluate chemical kinetic data on stratospheric reactions including especially those involving molecules emitted by supersonic transports cruising in the stratosphere.

Approach

The Climatic Impact Assessment Program of the Department of Transportation was charged with determining the potential ecological impact of propulsion effluents from fleets of supersonic transports flying the stratosphere. For its work the program drew on ten U. S. Federal departments and agencies and seven in other countries. Some one thousand scientists and engineers contributed to the technical outputs.

Stratospheric chemistry involves fifty or so molecules and free radicals, present at the part per million concentrations level or less, that can interact in 150 to 200 chemical reactions and photodissociation processes. The principal interest has been in how these reactions control the amount of ozone in the stratosphere, thereby determining the intensity of ultraviolet light that reaches the earth's surface.

For simple chemical models (minimal meteorology) the following types of data are needed:

1) The chemical mechanism, i.e., the specific chemical and photochemical processes that should be included to make the outputs meaningful.

2) The rate constant (as a function of temperature) for each elementary chemical reaction in the mechanism.

3) The optical absorption cross section for each molecule that can be decomposed by ultraviolet light.

4) The efficiency of photodissociation (quantum yield) for each molecule that absorbs u.v. light.

General questions asked by the CIAP managers are:

a) What chemistry is important and what can be ignored?

b) What is known about these chemical reactions; for which are there usable data and for which are measurements needed?

c) Which laboratories have the capability for making the measurements?

These questions were answered by kineticists and photochemists in the NBS Physical Chemistry Division.

The needs of CIAP for chemical data were extensive and varied. They were met in several ways. First a survey was made of papers on stratospheric chemistry to determine which reactions were important and what new measurements were needed either to improve the accuracy or to fill gaps in the data base. Second, a workshop for chemical kineticists and atmospheric modelers was held at NBS in the fall of 1972. This provided a forum for modelers to describe their needs and experimentalists to outline measurements that could be made in the near future. Third, as indicated in the previous section, an initial table of rate data was developed by the CIAP Chemistry Panel. Fourth, a data evaluation program was mounted at NBS to extend these tables and keep them up to date. Four editions of the tables were issued. The work involved scientists both at NBS and in other laboratories[1] the results being compiled and distributed by the Center. Fifth, this evaluation activity was supplemented by compilations of new data, not yet evaluated.

All of this material was distributed by the Center in a series of reports[1-11] and was made available to the general public as NBS Technical Note 866.

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[1] R. J. Cvetanovic, T. Slanger, K. H. Welge, W. H. Breckenridge, J. Troe, D. Drysdale, J. Heicklen, D. L. Baulch, D. G. Horne, D. Stedman, R. T. Watson.

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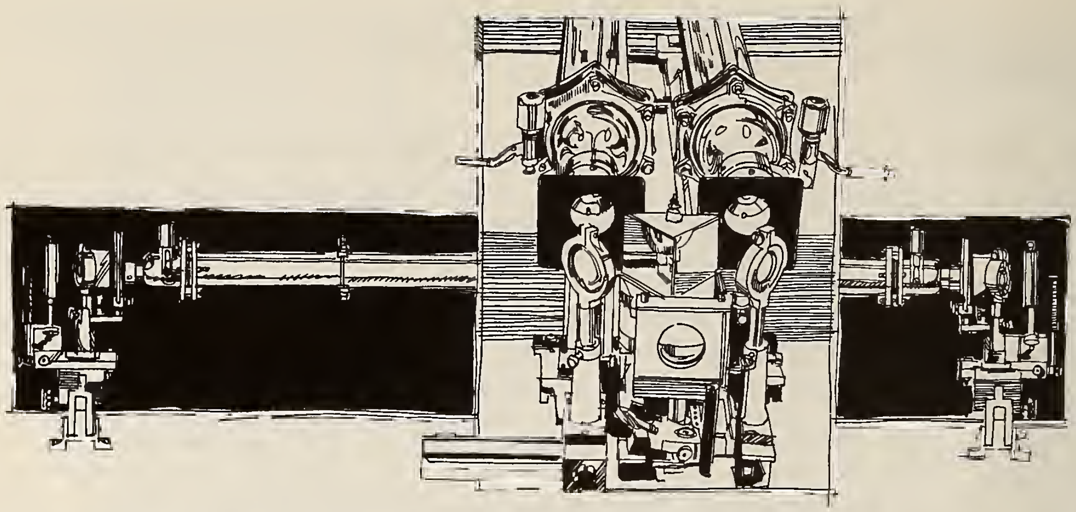
[2] NBS Reprots and publications in the NBSIR series that are still in print may be obtained from the Chemical Kinetics Information Center, NBS, Washington, DC, 20234.

12. A Computer Program for Solving Systems of Chemical Rate Equations

Project Leader: R. L. Brown, Physical Chemistry Division

A chemical language processor has been developed which simulates the generation of a computer code for a particular set of chemical rate equations. This code is then used by an efficient integrating algorithm to solve the resulting set of coupled ordinary differential equations. The program is applicable to spatially homogeneous, isothermal chemical systems. Reactions are entered in the general form $A + B \rightleftarrows C + D$, where any chemical name having up to 10 characters can be used. Three-body reactions, like $A_2 + M \rightleftarrows A + A + M$ can always be written in the general form provided the concentration of the third body can be considered to remain constant during the course of the reaction. Three-body reactions of the form $A + B \rightleftarrows C + D + E$ must be written as two separate two-body reactions. For mechanisms entered in this form only a simple program is required to calculate the time derivatives of all the chemical species and the Jacobian matrix for the set of differential equations. In its present form, systems can have a maximum of 50 species and 200 reactions. This is not a fundamental limitation. It can be used for larger systems if several array dimensions specifications are changed.



13. Ultraviolet Ozone Photometry

Project Leader: Arnold Bass, Physical Chemistry Division
Other Personnel: Al Ledford

Objectives

The objective of this work is to provide a facility for calibration of atmospheric ozone monitoring instruments by use of ultraviolet absorption photometry. Measurements are required in the concentration range of 50-500 ppb with an accuracy of 95% or better.

Approach

Recent controversies over the accuracy and reproducibility of iodometric calibration procedures for atmospheric ozone monitoring instruments have led to the proposal of ultraviolet absorption photometry as an alternative calibration method. In order to examine the nature of these discrepancies it is planned to intercompare the various methods in use for ozone concentration--iodometry, gas phase titration, and ultraviolet absorption photometry. The photometric measurement will be made by using a double-beam photometer based on the application of Beer's Law to the absorption by ozone of 253.7 nm radiation. The intercomparison with the other measurement methods will be done by using a commercial ozone monitor as a transfer instrument.

Progress

A double-beam photometer has been designed and constructed. The sample path length in this instrument is approximately 300 cm. The instrument measures changes in ozonized-air sample transmissions of mercury radiation at 253.7 nm where the photoabsorption cross-section of ozone has been well determined. The background mercury radiation is filtered by two narrow-band interference filters. The light is collimated and passed through a beam splitter which passes approximately equal intensity beams through the two absorption cells. Clean air flows through one cell into the ozone generator and then the ozonized air flows through the second cell. The light beams emerge from the cells and are recombined in the face of a photomultiplier tube used in the photon counting mode. A rotating chopper allows the two beams to be detected sequentially so that the transmission of the two cells may be directly observed.

The entire system has been assembled and preliminary measurements have been made. At the 100 ppb level the standard deviation of the mean of several measurements is approximately 5 ppb.

Future Plans

Future work will proceed as follows:

1) After completing some modification of the mercury lamp, the photometer measurements will be compared with the measurements of ozone concentration by iodometry and by gas phase titration. The photometer will then be available for intercomparison with ultraviolet photometers in other calibration laboratories;

2) The gas-handling system of the photometer will be modified so that it will be possible to perform gas phase titration measurements in the photometer. The titration reaction of ozone with nitric oxide (NO) produces NO_2. We will measure the concentration of the NO_2 produced by absorption photometry at 435.8 nm. If this measurement is made with sufficient accuracy, it can provide an independent method for the calibration of SRM samples of NO.

14. Gas Standards for Air Pollution Analysis

Project Leaders: J. K. Taylor and E. E. Hughes, Analytical Chemistry Division

Other Personnel: W. D. Dorko, B. C. Cadoff, W. P. Schmidt, R. J. Marinenko, D. G. Friend, S. Meeks, E. Scheide, R. H. Johns (ASTM), E. R. Deardorff, D. G. Friend, B. Greifer, K. Heinrich, R. Myklebust

Objective

This project is concerned with the development of Standard Reference Materials for air pollution analysis and the provision of traceability of all air pollution measurements, including those relating to the occupational environment, to a common set of analytical standards.

Approach

Research is conducted to develop or to improve techniques for preparation of primary gas standards by gravimetric, volumetric and manometric techniques. Instrumental methods will be developed for intercomparison of primary standards and with SRM's to establish the certification levels of the latter. Absolute methods for the analysis of gaseous mixtures will also be developed where possible. Studies will be made of the stability of gas mixtures, as this affects their usefulness as reference standards. The scope of the program includes measurements in the ambient air, of source emissions, and of the workplace atmosphere.

Progress

14.1 Ozone, Sulfur Dioxide and Nitrogen Oxides

Ozone Reference Standards

An investigation has been in progress to evaluate ozone generators as potential Standard Reference Materials. This includes a study of factors affecting their performance, and methods of calibration. The gas phase titration technique, using SRM nitric oxide-nitrogen as a reagent has been studied as an independent method of calibration of generators. Coincidentally, the stoichiometry of the neutral buffered potassium iodide (NBKI) reference method has been investigated.

The effects of temperature, oxygen content of the air, flow rate, and voltage fluctuations of the UV lamp have been studied and found to be consistent with predictions from the physical processes involved. The effect of humidity in the air to be ozonized was studied in detail and found to be significant. Reductions in ozone production in moist air as compared with dry air amounted to 6 percent and 13 percent when the relative humidity was 50 percent and 95 percent, respectively. However, no significant change in concentration was found when moisture was introduced into air already containing ozone.

Studies to evaluate the effect of atmospheric pressure on the production of ozone by the generator have not yet been undertaken and need to be done.

The gas phase titration (GPT) technique has been developed so that it can be used as an independent method for calibration of a laboratory standard ozone generator. This involves the reaction of ozone with nitric oxide of known concentration and measurement of the reduction in NO concentration due to this reaction. A precision gas dilution system utilizes SRM nitric oxide-nitrogen mixtures as the reagent so that calibration of a generator with reference to this SRM is possible.

Extensive intercomparisons have been made between the NBKI, the GPT, and ultraviolet absorption techniques. The UV measurements have been made with a commercial instrument. It was found that the NBKI method yielded results that were in general equal to or higher than the GPT. The UV method using the unmodified commercial instruments gave results that were 20-30% higher than the GPT.

The NBKI method was investigated in some detail in terms of the effects of sample flow rate, the time between completion of sampling and measurement of the iodine produced, the strength of the solution relative to KI, and to minor difference in operator technique. It was found that: (a) Variations in sampling time had little effect (less than 3%) as long as total sampling time was held to 10 minutes or less; (b) Variations in sampling rate had no effect between the limits 0.5-1.5 l min^{-1}; (c) The concentration of KI in the reagent had a great effect on the absorbance of the solutions after ozone collection. Under identical analytical conditions, 10% KI reagent yielded a 12% higher absorbance reading than 1% KI reagent; (d) Minor operator variables, such as different techniques for rinsing and drying impingers, length of time between sampling and reading the absorbance, and even differences in impingers yielded differences in results as 10% or greater.

Neither the chemical method nor the gas phase titration is a simple technique in execution and neither is particularly satisfactory for routine calibrations unless the laboratory has had considerable experience in its use. Accordingly the need for an ozone generator to serve as a calibration source is emphasized.

An important practical matter undergoing investigation is the long-time stability of the NBS ozone generator. The information being obtained will answer questions on the frequency of recalibration and the expected service life of a generator.

The UV lamps in use at present appear to produce decreasing amounts of ozone as a function of the number of hours the lamp has been in operation. The decrease is about 1% per 100 hours of operation.

Electrolytic Generation of Ozone

A novel technique for the generation of ozone by electrolysis of water has been investigated in a preliminary manner. Large amounts of ozone can be generated by electrolysis of perchloric or sulfuric acid solution at reduced temperatures. The amount of ozone produced is dependent on the current density and the temperature of the electrolyte. Several cells were designed and built which produced ozone in small quantities and by sweeping air through the cell it was possible to produce concentrations in the range of 0 to 1 ppm.

Preliminary results indicate that it may be possible to construct a cell capable of producing reproducible quantities of ozone in this range. Currently it appears that the concentration on a day to day basis, can be reproduced to about ± 5% of the amount. It is necessary to operate the cell at 0°C and to control the current to rather close limits to achieve the stated degree of reproducibility.

Further work is anticipated, which may improve the reproducibility.. Such factors as current control, internal cell temperature control, dissolution of ozone in the electrolyte and modification to the electrode to eliminate large bubble formation will be investigated.

Sulfur Dioxide Reference Materials

The stability of sulfur dioxide-air mixtures at stationary source concentration levels has been under investigation for several years. Samples contained in mild steel cylinders exhibit reasonable stability after an initial conditioning period. Initially, rapid and unpredictable changes in concentration occur, followed by a gradual attainment of equilibrium. While standards of this kind would be usable they would require individual calibration and periodic reevaluation to insure that stability has been reached.

The recent availability of specially treated aluminum cylinders, which have been found satisfactory for several reactive gas mixtures, suggested a possible alternative to mild steel. Consequently, five cylinders at each of the concentration levels of 500, 1000, and 1500 ppm were purchased. Analyses over a period of six months indicated excellent stability. Variation in concentration observed during the six month period lie within the error limits of the method of analysis. The stability of the samples and the accuracy with which the concentration can be measured are such that no problems are anticipated in the production of SRM's of these materials.

Consequently, a set of commercially prepared samples of sulfur dioxide in nitrogen consisting of twenty-eight samples each at concentration of 500, 1000, 1500 and 2500 ppm were analyzed. The analysis was performed using a modification of the peroxide method in which the sulfur dioxide is collected in a dilute solution of hydrogen peroxide in which it is oxidized to sulfuric acid and is subsequently titrated with standardized base.

The technique was independently validated using a technique in which the sulfur dioxide is oxidized to sulfate in peroxide and is then reacted with barium chloride to form the insoluable barium sulfate. The barium sulfate is then determined gravimetrically. The results of the two methods agreed well within limits of one percent.

The precision with which the sulfur dioxide could be determined in a sample, the agreement of the two methods, the uncertainty in standardization of the base and the uncertainties in the measurement of the volume of the gas sample resulted in a total uncertainty in the concentration of any sample of about one percent.

These samples are now available as Standard Reference Materials 1661, 1662, 1663 and 1664 which have nominal concentration of sulfur dioxide of 500, 1000, 1500 and 2500 ppm respectively.

Nitrogen Dioxide Permeation Tubes

Over one hundred nitrogen dioxide permeation devices (see figure 14.1.1) have been sold by the Office of Standard Reference Materials. These devices, SRM #1629, were fabricated and calibrated at the National Bureau of Standards. The sales records indicate a continuing need for these devices at a rate of about 50 per year.

Investigation is continuing concerning the life expectancy of these devices to increase the period of certification to a period greater than 6 months.

Automotive Standard Reference Materials

This project was concerned with the development of a series of Standard Reference Materials useful in the measurement of emissions from mobile sources. The experimental work included investigation of techniques for stabilizing the composition of the gas mixtures in high pressure cylinders, the preparation of specifications by which the mixtures can be produced by commercial suppliers, and the development of measurement techniques by which the SRMs can be intercompared with primary standards produced in the NBS laboratory. A further outcome was the design and construction of a semi-automated analytical system for intercomparison of the composition of gas mixtures.

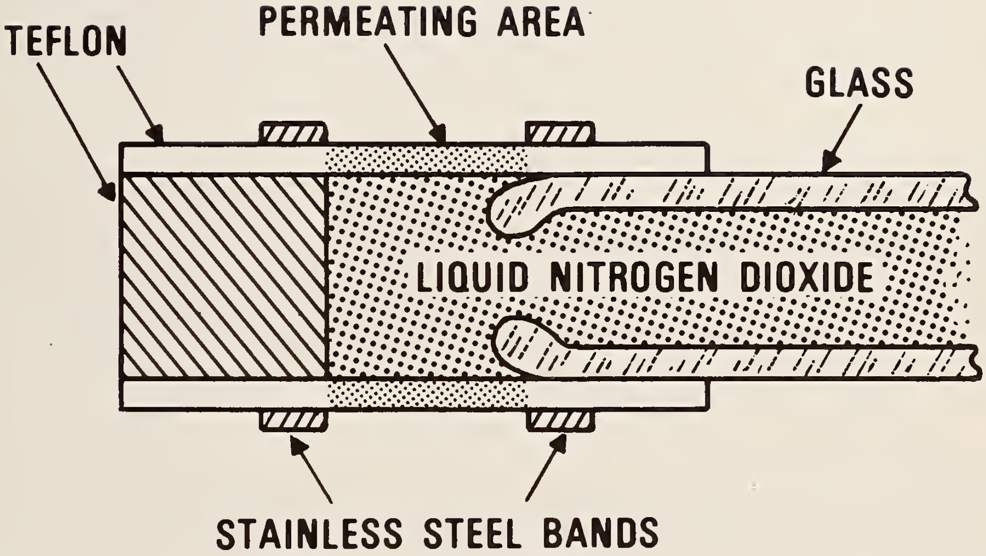


Figure 14.1.1 Nitrogen Dioxide Permeation Tube

The SRMs consist of a series of four binary gas mixtures, namely: propane-air; carbon monoxide-nitrogen; nitric oxide nitrogen; carbon dioxide nitrogen. The propane and the carbon dioxide mixtures were found to be stable in mild-steel cylinders. Coating the inside of steel cylinders with a thin layer of ceresine wax was found to provide long-term stability of carbon monoxide-nitrogen mixtures.

A pre-treatment process was specified for the nitric oxide mixtures. This consists of an initial conditioning (soak) of the mild steel cylinder with a mixture of approximately twice the concentration of the gas that it will finally contain. After standing for one week, the conditioning mixture is pumped out and the final mixture is introduced. This process results in adsorbtion of some nitric oxide on the walls of the cylinder as evidenced by the fact that some of this disorbs during blowdown as the pressure in the cylinder approaches atmospheric. However, no changes in concentration were observed as long as the pressure in the cylinder is greater than 400 psi.

The laboratory primary standards are made in stainless steel cylinders by a gravimetric procedure to a relative accuracy of 0.1 percent. Intercomparisons of these with the SRMs is accomplished as follows: For propane - gas chromatography using the flame ionization detector; for nitric oxide - chemiluminescent measurement; for carbon monoxide and carbon dioxide - gas chromatography using the flame ionization detector, after reduction of methane.

Techniques were also developed for preparation of the primary standards and for the determination of impurities in both the SRMs and the pure gases from which the primary standards are produced.

A novel semi-automated analytical system was designed and constructed for intercomparisons of each of these following gas mixtures with corresponding primary standards: Propane-air; carbon monoxide-nitrogen; carbon dioxide-nitrogen. The system uses the flame ionization detector as the sensor and includes a catalytic reduction system for conversion of the oxides of carbon to methane, prior to measurement.

The final outcome of this project has been the certification and issue of the following Standard Reference Materials:

1665	Propane in air, 2.8 ppm
1666	Propane in air, 9.5 ppm
1667	Propane in air, 48 ppm
1668	Propane in air, 95 ppm
1669	Propane in air, 475 ppm
1673	Carbon dioxide in N_2, 0.95%
1674	Carbon dioxide in N_2, 7.2%
1675	Carbon dioxide in N_2, 14.2%
1677	Carbon monoxide in N_2, 9.74 ppm
1678	Carbon monoxide in N_2, 47.1 ppm
1679	Carbon monoxide in N_2, 94.7 ppm
1680	Carbon monoxide in N_2, 484 ppm
1681	Carbon monoxide in N_2, 947 ppm
1683	Nitric oxide in N_2, 50 ppm
1684	Nitric oxide in N_2, 100 ppm
1685	Nitric oxide in N_2, 250 ppm
1686	Nitric oxide in N_2, 500 ppm
1687	Nitric oxide in N_2,1000 ppm

The gas mixtures are prepared by commercial suppliers, according to NBS specifications. Each SRM cylinder is individually calibrated at the National Bureau of Standards with respect to NBS primary standards. The certified accuracy of the composition is generally one percent, relative. The SRM certificate contains the composition of the specific cylinder and describes the conditions of preparation and use.

Reference Materials for Collaborative Tests of ASTM Air Quality Methods [1]

A three year program for the development of test materials for the collaboration tests of certain ASTM standard methods was completed. The work was done by Dr. Richard H. Johns, Research Associate, sponsored by the American Society for Testing and Materials. Personnel of the NBS Air and Water Pollution Analysis Section cooperated. The collaborative tests were conducted by ASTM in an activity known as Project Threshold. Both ambient levels and stationary source measurement methods were tested.

Reference materials developed or adapted to these collaborative tests included: SO_2 and NO_2 permeation tubes; ozone generators; potassium sulfate (sulfate measurements); neutral density filters; dust-fall composition standards; materials for particulate and vaporous lead in the atmosphere. The materials were used as quality control samples to check analytical accuracy or were injected into stacks or ducts as spikes to check both sampling and analytical measurements. Techniques for spiking were developed as part of the project.

14.2 Industrial Hygiene Reference Standards

The Occupational Safety and Health Act requires that national standards be established for toxic or hazardous substances in the industrial environment. OSHA must set the standards, provide regulatory surveillance, and certify instrumentation used by industry for compliance testing. NIOSH which is responsible for research in support of the OSHA mission has requested the assistance of NBS in developing analytical procedures and calibration techniques to be used by that agency in discharging its responsibilities. Traceability to NBS is a key consideration, and the techniques are also expected to be used by industry and equipment suppliers in verifying the performance of their instruments and quality control measures.

The methods will be relatable to SRM's as far as possible. The development of new SRM's where no other avenue of establishing traceability is available is a further aim of this project. The development of analytical techniques and sampling procedures in specific cases is a logical extension of this program.

Toxic Materials [2]

A number of materials were prepared as collaborative test samples and some of them have been precursors of Standard Reference Materials. Those that have appeared to date are described below.

SRM 2671	Freeze-Dried Urine Certified for Fluorine
SRM 2672	Freeze-Dried Urine Certified for Mercury
SRM 2675	Beryllium on Filter Media
SRM 2676	Metals on Filter Media (Pb, Cd, Zn, Mn)

SRM 2671 consists of two freeze-dried samples of human urine containing low (0.8 mg F^-/ℓ) and elevated (7.1 mg F^-/ℓ) levels of fluoride, respectively, when reconstituted with pure water. SRM 2672 is a similar set of samples containing low (0.05 mg Hg/ℓ) and elevated (0.29 mg Hg/ℓ) respectively, when reconstituted. The samples were developed primarily for the industrial hygiene analyst in connection with measurements of workers to these particular toxic substances.

SRM's 2675 and 2676 consist of membrane filters upon which have been deposited known and carefully reproduced quantities of salts of the respective metals. Three levels of metal content have been deposited in each case to simulate the amounts collected under typical conditions when the workplace atmospheric concentrations are near the detection level of commonly used industrial hygiene measurements, at the threshold, and well above the threshold level.

When the samples are used as a series, the analyst may discover whether the techniques he is using give reliable results or are biased by a constant factor or by a constant amount.

Work is in progress to produce a similar set of filters on which are deposited mixtures of quartz and clay. The target values are as follows (μg/filter):

	Blank	No. 1	No. 2	No. 3
Quartz	0	30	80	200
Clay	400	370	320	200

The filters were prepared in two steps in which the quartz was deposited, followed by deposition of the clay. This permitted measurement of the quartz or randomly selected filters by x-ray fluorescence (non-destructive), followed by chemical analysis of the same filters. As a result, homogeneity could be checked by true techniques, while the method of preparation and the chemical analysis provided independent estimates of the quartz content of the filters.

The filters are expected to be available for distribution on or about October 1, 1976, as SRM 2679, Quartz on Filter Media.

Adsorption Tubes [3]

Previous work at NBS has developed procedures for deposition of known amounts of organic solvents in charcoal tubes, such as are used for personal sampling in the work-place atmosphere. The technique makes possible the production of tubes with levels precise and accurate to ± 2 percent of the amount present. The availability of these tubes should greatly increase the measurement accuracy. Standard Reference Materials are now in the process of preparation and certification with the following target values(μg/tube):

Solvent/Tube	1	2	3	4
Benzene	16	64	256	960
Xylene	43	303	2170	13020
p-Dioxane	18	144	1080	7200
Ethylene	101	404	1616	6060
Chloroform	122	488	1952	7320
Trichloroethylene	268	1074	4296	16110
Carbon Tetrachloride	31	126	504	1890

Gas Blending System

In an Interagency Agreement with NIOSH, a system has been constructed to prepare mixtures of gases in which one component may be present at concentrations variable from several percent to a part per million. The starting materials may be either a pure gas, an organic liquid, or a gas mixture of an intermediate concentration. The system is intended to produce large volumes, 5 l/m, at a constant concentration for a period of 24 hours. The system will be used to calibrate gas detecting instruments and devices by the National Institute for Occupational Safety and Health.

The system consists essentially of flow control devices which allow the mixing of two gas streams in a predetermined and reproducible ratio. Two or more stages of dilution may be employed by transferring the gas mixture from one stage to the next with small non-contaminating pumps. The starting materials may be a liquid with which a gas stream is saturated or a pure gas obtained from a cylinder under pressure.

The system is quite flexible in that the components can be arranged in different configuration to produce a wide range of concentration of a substance in air from 10% to 1 ppm starting with the pure substance and a diluent gas.

Reproducibility is excellent and is assured by using calibrated mass flow meters. In practice this accuracy is assured by periodi calibration of each flow measuring device with a wet-test meter which in turn has been calibrated by passing a measured weight of gas through the meter. Mixtures can be prepared with an accuracy of between 0.2 and 1%, depending on the extent of dilution and on the peculiarities of the particular gas mixture being prepared. The accuracy of mixing was confirmed by comparing the concentration of propane produced at various dilutions with Standard Reference Materials and other gas standards of known accuracy.

Several versions of the system are currently in use in the laboratories of the National Institutes of Occupational Safety of Health for use in calibrating gas detecting devices.

Gravimetric Analysis of Gas Mixtures [3]

A method has been developed for measurement of the concentration of gas mixtures by gravimetric measurement of the weight of a component collected on activated charcoal. The technique is potentially adaptable to any binary mixture containing a component adsorbable on charcoal and has been found useful for analysis of those containing the vapors of organic solvents.

A measured volume of the gas to be analyzed is drawn through a tube containing activated charcoal, which has previously been equilibrated to constant weight. A system, utilizing a critical orifice, has been developed to maintain a steady rate of flow. Sufficient sample is taken to produce a weight change of several milligrams for the charcoal adsorber. Measurements of styrene, toluene, benzene, ethylene dichloride, chloroform, and methylene chloride have shown that a precision of 1 percent can be obtained at the 50 ppm level.

Solid Sorbent Collection Systems [4]

Another NIOSH sponsored project was concerned with development of sampling systems based on the collection of the component of interest on a solid sorber. The sorption can be either physical or chemical in nature.

Furthermore, the sampling systems need to be applicable as personal samplers to measure a time-weighted-average exposure, and compatible with commonly available analytical measurement methodologies.

A very effective sorbtion system was developed for collection of hydrogen fluoride. The collector is packed with crystals of sodium acetate which trap the stronger acid as sodium fluoride, while liberating the weaker acetic acid. By rise of the fluoride ion selective electrode for measurement, the combination of collector-analyzer is very specific.

A similar system was developed for measurement of hydrogen cyanide exposure of industrial workers. The collector consists of flakes of sodium hydroxide contained in a plastic adsorbtion tube. Again selectivity is achieved by using the cyanide ion selective electrode for the analytical measurement.

Quality Control Analyses

NBS has assisted NIOSH during both FY 1975 and FY 1976 in connection with the latter's quality control program. The Chemical Reference Laboratory of NIOSH periodically issues samples in its Proficiency Analytical Testing Program (PAT). NBS has been analyzing selected samples from these series for lead, cadmium, and zinc; for quartz; and for organic solvents adsorbed on charcoal. These values are used by NIOSH to evaluate the PAT samples and particularly to assist them in setting control limits for certification of laboratory efficiency.

It is expected that the availability of NBS SRM's for many of these materials will minimize the frequency of test samples required to establish laboratory proficiency.

Vinyl Chloride Reference Materials [5]

The objective of this work was to provide reference materials for use in an EPA program to monitor the vinyl chloride concentration in the ambient air. Compressed gas mixtures of vinyl chloride were needed for calibration of instrumentation. Quality control samples were also desired consisting of charcoal tubes with known amounts of vinyl chloride deposited upon them, corresponding to that obtained by sampling the atmosphere at three different concentration levels.

Fifteen cylinders containing mixtures of vinyl chloride in nitrogen were analyzed. These cylinders had been ordered by EPA from a commercial supplier who shipped them to NBS enroute to final delivery to EPA. The nominal concentration levels were as follows: 2 cylinders at 900 ppm; 6 cylinders at 40 ppm; 7 cylinders at 1 ppm.

The vinyl chloride content was determined by gas chromatographic analysis by comparison with primary standards prepared at NBS.

The chromatograph used was a commercial model with dual columns and dual flame ionization detectors. The column used was 3.12 mm (1/8") OD, 1.8 m (6') long packed with Poropak Q and operated at 100°C. A gas sampling valve with 5 cm^3 sample loops was used for sample injection. The samples and standards were compared by measuring the respective peak areas using an electronic digital integrater.

The mixtures of vinyl chloride used as calibrants were compounded in our laboratory by partial pressure measurements to nominal concentrations of 2, 10, 50, 100, and 1000 ppm by volume. The lower concentrations were made by successive dilutions of the higher concentration mixtures. The calibrant mixtures were compared with existing Standard Reference Material propane mixtures using the gas chromatograph and the relative FID response factors for vinyl chloride and propane. These mixtures had been prepared previous to this project as part of a study to evaluate the stability of vinyl chloride mixtures when stored in cylinders.

The samples at the 900 and 40 ppm levels were compared with the vinyl chloride calibrants at these levels. The relative uncertainties in the calibrant mixtures were 1.5 percent and 2.0 percent, respectively. The samples at the 0.9 ppm level were analyzed using the calibrants at 2 and 10 ppm with relative uncertainty in the calibrants of 2.5 percent.

Charcoal tubes were prepared upon which known amounts of vinyl chloride were deposited to serve as analytical quality control standards. The amount deposited corresponded to that which would have been collected during 24 hours at a sampling rate of 0.2 l/min, for several concentration levels of vinyl chloride. The concentration levels were first set at 0.1, 1.0, and 5 ppm respectively and a few pilot tubes were prepared on this basis. The levels were later modified to 0.014, 0.10, 1.0 ppm respectively, and most of the tubes were prepared accordingly.

The charcoal tubes were supplied by EPA. They consisted of glass tubes approximately 1 cm in diameter and 16 cm in length which contained approximately 13 cm of charcoal of 8-16 mesh size. Glass wool plugs had been inserted in each of the tubes, which had been constricted, to hold the contents in place. Rubber septum plugs were inserted in each end of the tubes to prevent circulation of air. The tubes were covered with aluminum foil to exclude light during storage.

Each tube, when received, had been given a code number which was used to identify it.

The tubes were randomly selected from the lot used for atmospheric monitoring and more indistinguishable from others except by reference to the code number. They could therefore serve as blind samples for quality control purposes.

The analytical standards were prepared by a method developed at NBS under an Interagency Agreement with NIOSH [3]. It consists essentially of drawing a measured volume of gas through the tubes which are totally immersed in an atmosphere of gas of known composition. The tubes are attached to matched critical orifices mounted on a circular manifold. By application of a vacuum to manifold the same volume of gas is drawn through each orifice. The average flow rate for the critical orifices used was 0.9139 liter/min and no orifice deviated by more than 0.8 percent of this value.

The manifold is covered with a bell-jar with a gas inlet and outlet to provide an ambient atmosphere of known gas composition. Twenty tubes can be prepared simultaneously.[3].

The amount of vinyl chloride deposited on a given tube can be calculated from the concentration of the gas mixture and the volume of gas which was drawn through it. The latter can be obtained from the length of time of the flow, the calibration data of the critical orifice, and application of the appropriate correction factor for the pressure drop of the particular tube.

Selected tubes from the lot were also analyzed, by gas chromatography, to verify the amount of vinyl chloride predicted to have been deposited. The method consists in desorbtion of the vinyl chloride from the charcoal, using a known amount of carbon disulfide and gas chromatographic analysis of the resulting solution. The chromatograph is calibrated with solutions of known concentration of vinyl chloride in carbon disulfide.

Altogether, 900 charcoal tubes were prepared with the amounts of vinyl chloride ranging from 12 µg per tube to 3600 µg/tube. The uncertainty of reported levels was estimated to be 2.5 percent.

Indirect Determination of Sulfate in Natural Waters by Ion Selective Electrode

The indirect determination of sulfate in natural waters (seawater and simulated rainwater) was accomplished by titration with lead nitrate solution using the lead ion-selective electrode as the titration sensor. The indirect determination of sulfate is based on the formation of $PbSO_4$ which is quantified by measurements with a lead electrode. The measurements were carried out in 80 percent isopropanol using a double-junction reference electrode. The data evaluation was performed by a Gran plot of the titration of sulfate samples with standard lead nitrate. Samples containing between 2 and 100 ppm sulfate concentration were analyzed directly, while samples of higher sulfate concentration were diluted prior to analysis. The seawater samples were diluted 100-fold prior to analysis. A summary of the results are presented in Tables 14.2.1 and 14.2.2.

Conclusions

Sulfate concentrations in natural waters as low as 3 ppm may be determined indirectly by using a lead ion-selective electrode. The accuracy, precision and length of time required to run the analysis compare very favorably with other techniques that are generally used for this determination and the range of samples that can be analyzed is broadened to include rainwater, brackish water and seawater. By repolishing the electrode frequently, rainwater and seawater samples may be analyzed directly with no sample pretreatment.

Survey of Analytical Methods [7]

A comprehensive report has been prepared which evaluates the capabilities of the presently available instrumental methods for determining traces of 27 important elements in a wide variety of industrial process fields and waste materials. The report was prepared by measurement experts in the NBS Analytical Chemistry Division and the evaluations are based upon literature surveys and their experience in environmental materials analysis. Extensive use is made of tabular format and the evaluations reflect cost-benefit considerations. Many references to the original literature are given.

Quality Control of Ambient SO_2 Measurements [8]

A set of reference materials was developed to serve for quality control and performance evaluation of measurements of ambient levels of sulfur dioxide by the pararosaniline (PRA) method. The materials consist of small quantities of sodium sulfite homogeneously mixed in pure mannitol which serves as an inert diluent. Such samples can be weighed out and dispensed in vials to simulate the amount of SO_2 collected during a 24-hour sampling period, for various levels present in the atmosphere.

Two batches, each containing 400 sets, of these materials were prepared for EPA for use in quality control assessments

TABLE 14.2.1

ANALYSIS OF SULFATE IN RAINWATER

Sample	(ppm) Added	Ion-Selective Electrode		Gravimetric		Turbidimetric	
		Found (ppm)	(Percent)	Found (ppm)	(Percent)	Found (ppm)	(Percent)
B	3.57	3.57±0.02	100.0±0.6			3.5 ±0.35	98.0±10.0
C	5.02	4.93±0.08	98.2±1.6				
D	10.00	10.12±0.13	101.2±1.3	10.03[b]	100.3[b]		
#400[a]	4.00	4.06±0.04	101.5±1.0				
#500[a]	8.33	8.24±0.08	99.0±1.0				

[a] Samples #400 and #500 were dilutions made from sample "D".

[b] Only one analysis was performed.

TABLE 14.2.2

SULFATE IN SEAWATER ANALYSIS[a]

Sample	SO_4 (mg/1)
1	2735
2	2683
3	2760
4	2785
Ave	2741 ± 44

[a] This analysis agrees very well with the value of 2717 ± 19 mg/ℓ (n = 10) reported by Luther and Meyerson [6] which was done by indirect polarography.

of laboratory performance. A set of 5 samples spanning the entire range of conceivable SO_2 levels. By the use of 5 samples covering the range both addition and multiplication errors can be identified. The chance for confusion of interpretation, resulting from an outlying sample is also minimized.

While the samples prepared in the above manner were of sufficient homogeneity for the intended purpose, it is recognized that the mixing of microgram amounts of a solid in gram amounts of a solid diluent is a difficult process. Accordingly, alternate approaches were tried. It was found that small volumes of the tetrachlormercurate (TCM) solution, the absorbtion solution for the PRA method, containing sodium sulfite can be freeze dried to provide test samples. Such solutions are quantitatively dispensed into ampoules, freeze-dried, and sealed under vacuum, preferably. The advantage of this technique is that the samples are more uniform which may offset the disadvantage of greater cost of preparation.

Samples made by either method are dissolved in a specific volume of TCM solution and analyzed in the same manner as a sample collected in an atmospheric impinger sampler. The samples may then be used to evaluate all aspects of the SO_2 measurement, except the actual sampling.

Source and Environmental Fate of Toxic Heavy Metals in a Defined Region

Objective

The purpose of this investigation is to develop and demonstrate an analytical methodology for ascertaining the mass balance of toxic heavy metals in Washington, DC, in order to identify the information base necessary to effectively limit and control population exposures in urban areas. The sources, sinks, and the movement into, within, and out of the DC metropolitan area will be considered. The analytical measurements necessary to obtain a mass balance will be established and tested using analytical data obtained by the DC Environmental Services laboratory. The project was initiated with funding for studies of mercury and was extended to include cadmium and lead.

Approach

This project will go through six phases before completion. These are listed below;

1. Literature Search
2. Sampling Site Determination and Evaluation
3. Sampling and Analysis Procedures
4. Data Collection
5. Data Evaluation
6. Final Report

Phases 1, 2 and 3 have been essentially completed. The data collection (phase 4) will begin during the next month.

Progress

A literature search has been conducted in order to determine the state-of-art in heavy metals analysis, especially the analysis of environmental samples for mercury, cadmium and lead. Reports have also been obtained concerning environmental studies of similar scope and objectives as this one done in other parts of the country. The literature has also been scanned for information concerning sampling and storage of environmental samples.

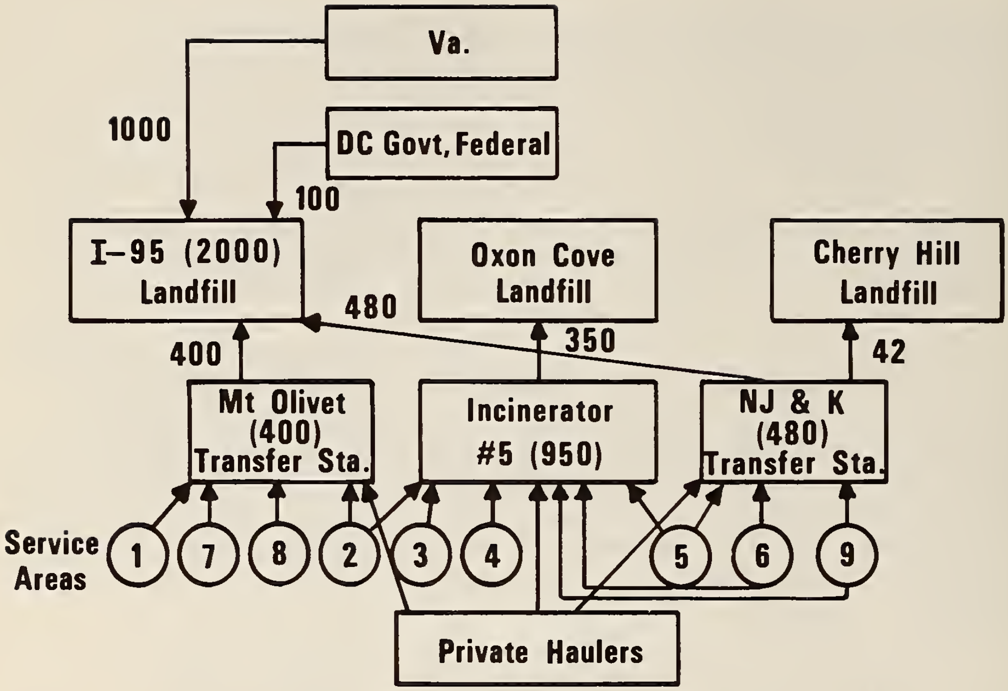
Solid waste, sewage and drinking water flow charts for Washington, DC have been drawn, and copies of these are included with this report (Figures 14.2.1 and 14.2.2). A sampling schedule has been devised and a map showing the sampling sites is also included with this report (Figure 14.2.3).

The air samplers are being constructed and the analytical and calibration techniques are being worked up for these samples.

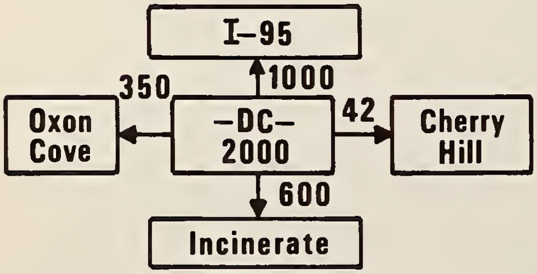
NBS standard reference materials have been sent to the Blue Plains laboratory for analysis and the results have been obtained and discussed. Several changes have been recommended and the Blue Plains analyst(s) will spend some time at NBS going over these procedures and obtaining additional specialized atomic absorption training.

Voluntary Standards Participation

A number of NBS scientists and particularly members of the staff of the Analytical Chemistry Division, participate actively in the program of work of ASTM committee D-19 on Water. Accordingly, a cost center was established during Fiscal Year 1976 to support this activity and to provide for more active participation where it is desirable to do so.



Total DC Solid Waste = 950 + 400 + 480 + 100 + 42 = 2000 tons/day



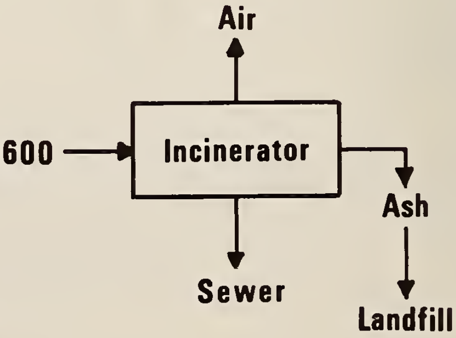


Figure 14.2.1 Solid Waste Flow Diagram

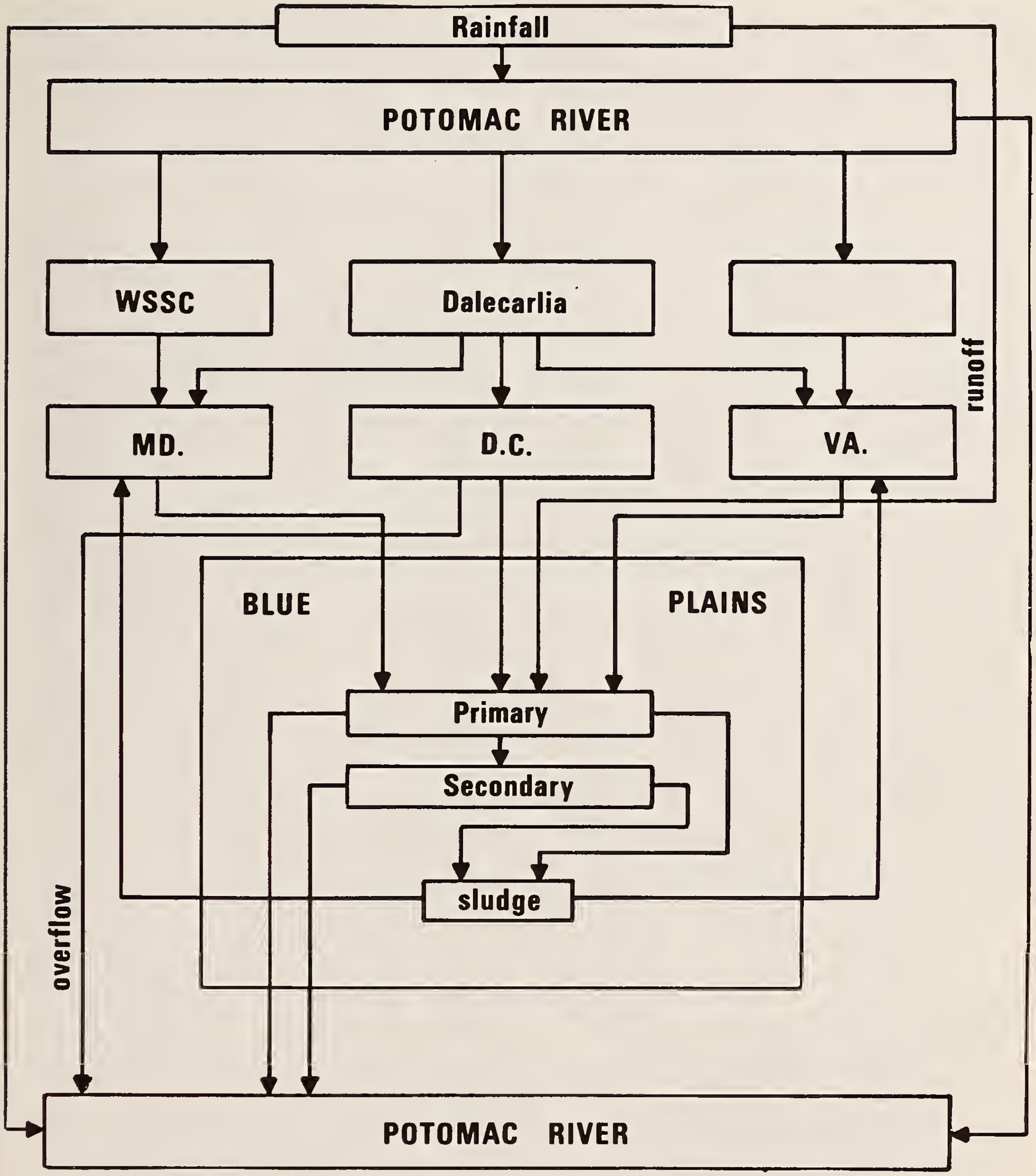


Figure 14.2.2 Water and Sewage Flow Diagram

Figure 14.2.3 Map showing sampling sites.

A total effort of approximately 0.4 man years was devoted to this activity, consisting of attendance at meetings, review of manuscripts, drafting of proposed standards, and participation in collaborative tests of proposed standard methods.

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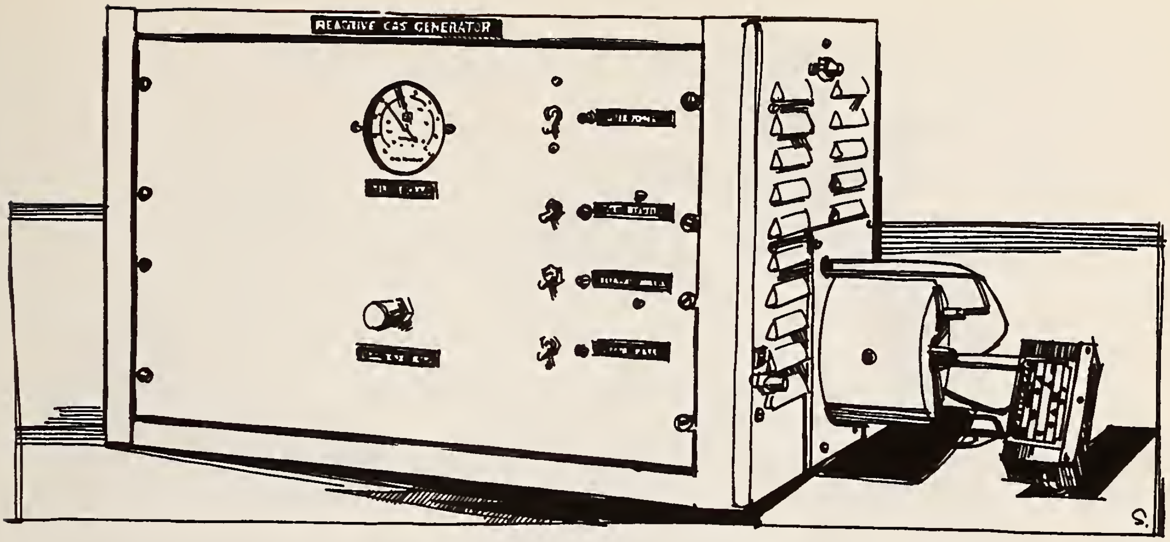

15. Calibration Standards by Thermal Decomposition

Project Leader: Wing Tsang, Physical Chemistry Division
Other Personnel: James Walker, Physical Chemistry Division and Douglas Cornell, Fairleigh-Dickensen University

Objective

a) To demonstrate the feasibility of generating dilute, known quantities of pollutant gases which are not readily contained in steel cylinders.

b) To construct an apparatus which will permit the continuous generation of dilute concentrations of pollutant gases.

Approach

Thermal decomposition of appropriate "parent" compounds. Construct a demonstration prototype.

Progress

Three reactive gas generators have been constructed and tested. One has been delivered to the Center for Fire Research and another to the Office of Air and Water Measurement. The reactive gases that can be generated by this instrument are $HCHO$, CH_3CHO, CH_2CHCHO, SO_2, HCN, and HCl. The specific reactions are

$$CH_2 = C(CH_3)CH_2CH_2OH \rightarrow iC_4H_8 + HCHO$$

$$CH_2 = CHCH_2CHOHCH_3 \rightarrow C_3H_6 + CH_3CHO$$

$$CH_2 = C(CH_3)CH_2CHOHCH = CH_2 \rightarrow iC_4H_8 + CH_2CHCHO$$

$$(CH_2)_3SO_2 \rightarrow c\text{-}C_3H_6 \rightarrow C_3H_6 + SO_2$$

$$CN\ COOC_2H_5 \rightarrow HCN + CO_2 + C_2H_4$$

$$cC_6H_{11}Cl \rightarrow c\text{-}C_6H_{10} + HCl$$

A large variety of other thermally stable pollutants can be generated in this manner. These include CO from the reaction

α-1-dicyclopentadienol → cyclopentadiene + butadiene + CO

and NO from the reaction

$$CH_3CHONOCHONOCH_3 \rightarrow 2CH_3CHO + NO$$

An unexpected application of the generator occurred in recent successful efforts in Herron's laboratory to calibrate mass spectral analyses of formaldehyde, a product of combustion and smog reactions.

Several papers have been published [1-4], others are being prepared [5,6] and a patent is being sought.

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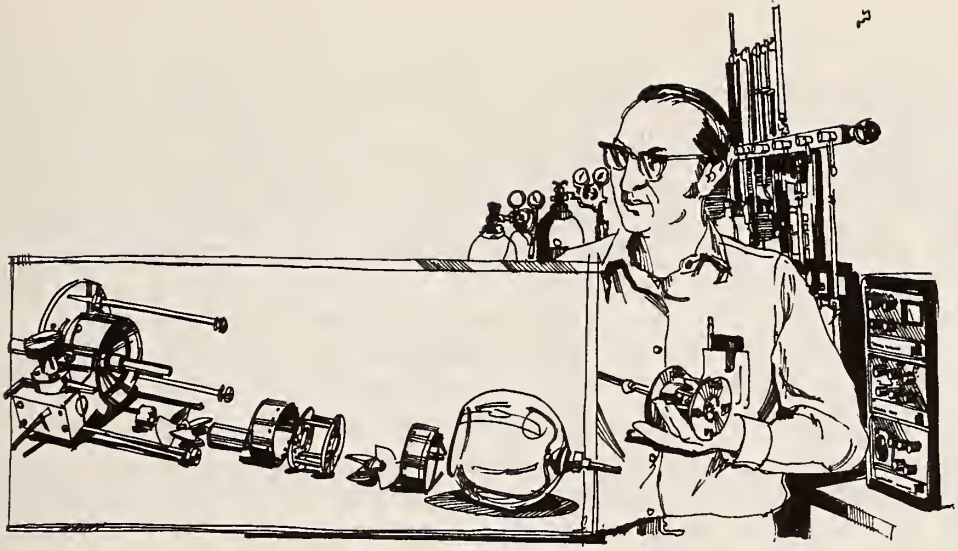


16. Gas Dilution Calibration Techniques

Project Leader: J. J. Ritter, Inorganic Materials Division
Other Personnel: N. K. Adams

Objective

To examine experimentally the capabilities and limitations of the NBS exponential dilution flask as a certifiable device for the rapid calibration of fast-response air monitoring equipment.

Approach

The performance of the NBS-developed exponential dilution flask (EDF) was evaluated by comparison to currently available propane-air Standard Reference Material (SRM) mixtures. Several operational procedures involving the NBS dilution flask were examined in an attempt to establish a realistic method for the use of the EDF in the calibration of a flame ionization detector (FID). The performance of the NBS-EDF was compared to that of a conventional EDF.

Progress

Several approaches were studied in the application of the NBS-EDF to the calibration of a FID. Two practical procedures were developed. The first involves the introduction of an approximately known quantity of pure calibrant gas into the operational dilution flask and utilizing the resultant data to compute the detector linearity factor, n. [The factor, n, is simply the ratio of the slope of a plot of the logarithm of the observed signal vs. time to the theoretical slope computed from the volume of gas involved in mixing and gas flow rate.] A single high-level response-concentration relationship $(\frac{S_o}{c_o})$ (within the concentration region covered by the dilution curve) for the FID is established with a propane-air SRM. All responses (S) above or below the SRM gas level can now be expressed in terms of calibrant concentration (c) by the use of the equation $S = \frac{S_o}{c_o^n} c^n$.

Typical results obtained by this procedure are given in Table 16.1.

Table 16.1 Comparison of FID Calibrations by SRM and EDF[a]

c_{SRM}	c_{EDF}	$^{a}c_{EDF}$
93.9	92.0	0.7
46.3	Calibration mixture	
9.51	9.62	0.05
2.96	2.97	0.05

[a] 46 ppm SRM used to establish a reference point on the exponential curve.

The second method requires the introduction of a precisely known quantity (N_o) of pure calibrant gas into the dilution flask and an integration of the area (A) under the resultant curve. The linearity factor (n) for the detector is obtained as before, the carrier gas flow rate (r) measured and the volume of carrier gas in the flask under actual operating conditions (V_m) must be determined. The response (S) is related to sample concentration through the following equation:

$$C = \frac{N_o}{V_m} \left(\frac{SV_m}{Arn}\right)^{\frac{1}{n}}$$

The latter technique does not require the use of a precalibrated SRM gas mixture, but necessitated the development of a precision sample introduction device to be used in conjunction with the EDF.

Comparative FID calibrations were conducted utilizing four propane-air SRMs and the NBS EDF operating with air as a carrier gas and measured amounts of pure propane calibrant. The results are given in Table 16.2.

From Table 16.2 it will be noted that all of the c values obtained from the EDF are consistently low compared to the certified SRM values. Investigations into probable causes for this, disclosed that the carrier air contained about 6% more oxygen than the SRM diluent air. Carrier air of comparable O_2 content was obtained and the calibrations were repeated. The results are shown in Table 16.3.

The data in Table 16.3 show that the agreement between the certified SRM values and the EDF values is now improved except at the high level where a bias still persists. The contents of the SRM cylinders were reanalyzed using gas chromatographic methods, and by comparison to standard gravimetric C_3-H_8-air mixtures, shown to be essentially unchanged. During the reanalysis it was also demonstrated that the use of the SRM delivery system did not affect the delivered propane concentrations.

The results of calibrations using the alternative method based upon an exponential curve and a single SRM calibration point on that curve are given in Table 16.2.

Table 16.2. Comparison of FID Calibrations by SRM and by EDF, Initial Results

c_{SRM} ppm C_3H_8 in air v/v	c_{EDF}	$^{a}c_{EDF}$
93.9	89.8	0.1
46.3	43.8	0.3
9.51	9.41	0.04
2.96	2.86	0.02

Table 16.3 Comparison of FID Calibrations by SRM and EDF[a]

c_{SRM}	c_{EDF}	$^{a}c_{EDF}$
93.9	90.4	0.8
46.3	45.4	0.3
9.51	9.48	0.11
2.96	3.01	0.05

[a] SRM diluent air and EDF carrier gas of comparable O_2 content.

A bias at the high propane concentration is again indicated. If the EDF were a significant contributor to this bias, one might logically expect the effect to be reflected in all c_{EDF} values. The results more directly suggest a possible alteration in FID linearity at relatively high propane concentrations. If this were the case, then one could expect the change in linearity to manifest itself in the slopes (k's) of the exponential curves in the 50-120 ppm region. However, a detailed examination of the slopes of the decay curves showed the k values to be identical (within the standard deviation) in the 100, 50, 10, and 3 ppm regions. We suspect that the difficulty may be related to differences in FID behavior whether subjected to a constant high propane level as in the SRM determinations or to transient propane levels as in the EDF experiments. Thus, the source of this bias becomes a problem for further investigations.

A conventional EDF of relatively advanced design was evaluated. Carrier gas flow rate, EDF gas temperature, EDF volume, EDF operating pressure, etc., were measured with the instrumentation normally used to monitor the NBS dilutor. The EDF was coupled to the same FID used in all previous work. The device was found to be exponential, (*i.e.*, a least-squares fit of log signal *vs*. time gave a reasonable straight line) and showed good slope reproducibility ($\sigma \sim 0.005$ k). However, the experimental slopes differed from those expected from $\frac{r}{V_m}$ by as much as 14%. This EDF, when used as recommended, is thus incapable of being used to assess detector linearity as described previously in this report. A realistic detector calibration must not only give a response-concentration relationship but also a measure of detector linearity.

Detector Linearity. The linearity (n) of the FID used in this work was determined from both the EDF experiments and from SRM data. For n_{SRM}, this involved least-squares fitting of six sets of data, each containing four points while n_{EDF} was obtained directly from the k and α values as described previously. The mean values and their standard deviations (σ, for a single measurement) are given below:

$n_{EDF} = 1.020$, $\sigma_{EDF} = 0.005$, 34 measurements (n_{EDF})

$n_{SRM} = 1.006$, $\sigma_{SRM} = 0.013$, 6 measurements (n_{SRM})

Student's t-test was employed to determine whether or not the mean values above are significantly different. For the present case

$$t = \frac{n_{EDF} - n_{SRM}}{\left(\frac{\sigma^2_{EDF}}{n_{EDF}} + \frac{\sigma^2_{SRM}}{n_{SRM}}\right)^{1/2}}$$

The above data gave t = 2.60, indicating that n_{EDF} and n_{SRM} are significantly different. It can be shown that when $t \geq 1.96$, the mean values are significantly different (95% probability), whereas when $t \leq 1.96$, the mean values are not significantly different.

The data associated with the 94 ppm SRM were eliminated from each of the six sets of data and the remaining three SRM points in each set were refitted by the least-squares method. The FID linearity (n_{SRM}) obtained from this procedure was 1.012 with $\sigma_{SRM} = 0.016$. The n_{EDF} and n_{SRM} values were subject to the "t" test with the result that t = 1.21, which indicates that the values for n_{EDF} and n_{SRM} are not significantly different.

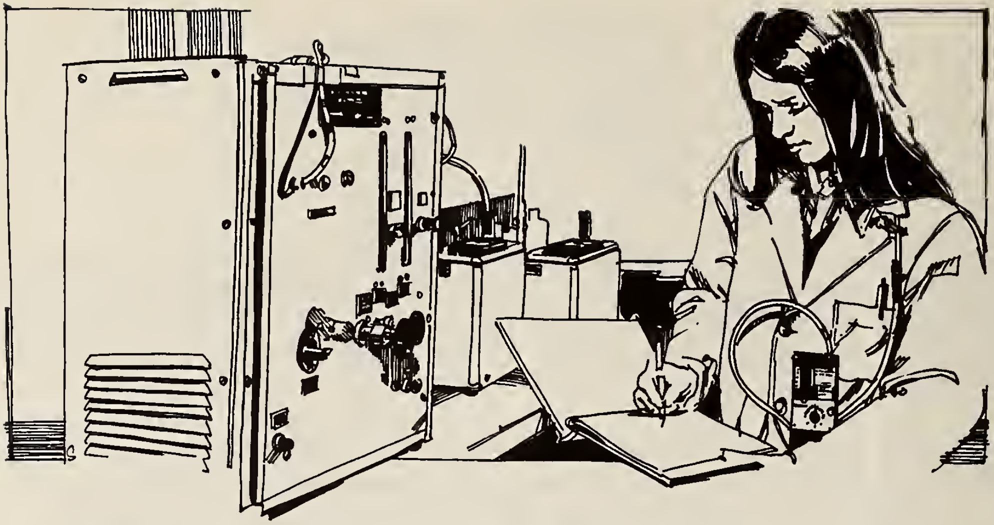
The statistical testing suggests the presence of a systematic error in n_{SRM}. This error arises from the signal (S) obtained from the 94 ppm SRM under our experimental conditions. Since the propane concentration of the 94 ppm SRM has been duly verified, we believe the error to originate in the FID. The presence of a systematic error has been previously noted in the calculation of c_{EDF} for the 94 ppm SRM.

Flame ionization detector calibrations performed with the type IV EDF have been shown to be repeatable to ±1%. It has been further shown that the FID can be calibrated in the 50- to 3-ppm region with acceptable accuracy without reference to any precalibrated gas mixture by charging the EDF with a minute quantity of pure calibrant gas. Although the potential of the EDF as a calibration device has been demonstrated, an extension of the verifiable calibration range would be highly desirable. Further work with the FID and with other detectors will assist towards the achievement of this goal.

The NBS exponential dilution flask design is protected by a U. S. patent (3,911,723). [1].

References

[1]. *Anal. Chem.*, 48, 612 (1976).



17. Piezoelectric Air Pollution Sensors [4-5]

Project Leader: Eugene P. Scheide, Analytical Chemistry Division

Objective

The objective of current research is to study the feasibility of using coated piezoelectric crystals as selective and sensitive environmental sensors.

Approach

The frequency of vibration of a piezoelectric sensor is dependent on the weight of the coating and the weight of the vapor adsorbed onto the coating. The concentration and/or total exposure of the pollutant is therefore measured by monitoring changes in frequency of the coated piezoelectric crystal detector. The sensor is quantitative and can be made selective by using selective substrates.

Progress

A film badge (dosimeter) has been developed and evaluated for the measurement of mercury vapor in industrial atmospheres. In the employment of personal environmental monitors in industrial hygiene analysis, a collection device is needed that is small enough to be worn on a worker's clothing and compatible with existing miniature air pumps. An alternative to the commonly-used solid state sorption tube is the piezoelectric crystal sensor. This is a gravimetric device in which the mass of material deposited or absorbed onto it is determined by measuring its change in frequency. By applying a substrate to the crystal that allows selective adsorption of the contaminant of interest the total exposure to this contaminant is determined from a calibration chart by measuring the frequency change of the crystal and the time of the sampling period. The sensor is very sensitive (lower limit ~10^{-12} g) and can be made selective for many substances by applying various selective substrates.

The piezoelectric sensor using gold as the selective substrate has already proven capable as an analytical tool for mercury analysis [1,2]. In the present application, however, the sensor is used as an integrating device to measure total exposure for a given time period. The sensor is small enough (1" x 1" x 2", and weighs less than 10g) to be worn in the breathing zone of an individual and used in conjunction with a miniature personal pump.

Figure 17.1 shows a picture of a piezoelectric crystal and the glass holder into which it is sealed, while the above sketch shows the sensor and pump in operation.

Air samples containing mercury vapor of known mercury concentration from a mercury vapor generation system [3] were drawn past the sensor using a miniature pump. The flow rate was varied between 20 and 250 cm^3/min and the sampling time was varied between 2 min and 8 hours. After sampling and frequency measurement, the mercury was desorbed from the sensor by placing the sensor in an oven at 150°C and passing clean, hot air over the sensor. The mercury is thereby desorbed from the gold surface and the sensor is ready to use again.

Figure 17.2 shows the response from sampling mercury vapor of 50 ng/l concentration. Three different sensors of different fundamental frequency were used. As can be seen, the higher the frequency the greater the sensitivity, but the range or adsorption capacity is less. Thus, higher frequency crystals can be used for grab samples, while lower frequency crystals can be used for 8 h exposures.

The reproducibility of replicate samples was ±5 percent.

The collection efficiency was studied as a function of flow rate. Even at the lowest flow rate studied (20 cm^3/ min) the collection efficiency was not 100 percent. This was proven by placing two sensors in series. The second sensor adsorbed mercury vapor in all cases indiciating low collection efficiency by the first sensor. Studies are still in progress in optimizing this parameter. However, the sensor can be used as is because the collection efficiency is constant, providing the flow rate is kept constant. Figure 17.3 shows the sensor response versus flow rate.

The cost of piezoelectric sensors, when produced in quantity, should approach that of the solid adsorbent collectors since the former can be re-used many times. The analysis time using piezoelectric sensors is much shorter and the analysis can be carried out by untrained personnel. The analytical instrumentation is also less expensive and can be used for the analysis of other gases once other selective substrates are found. The piezoelectric sensor is much more sensitive than most other techniques and can be used without time-consuming pre-concentrating steps before analysis.

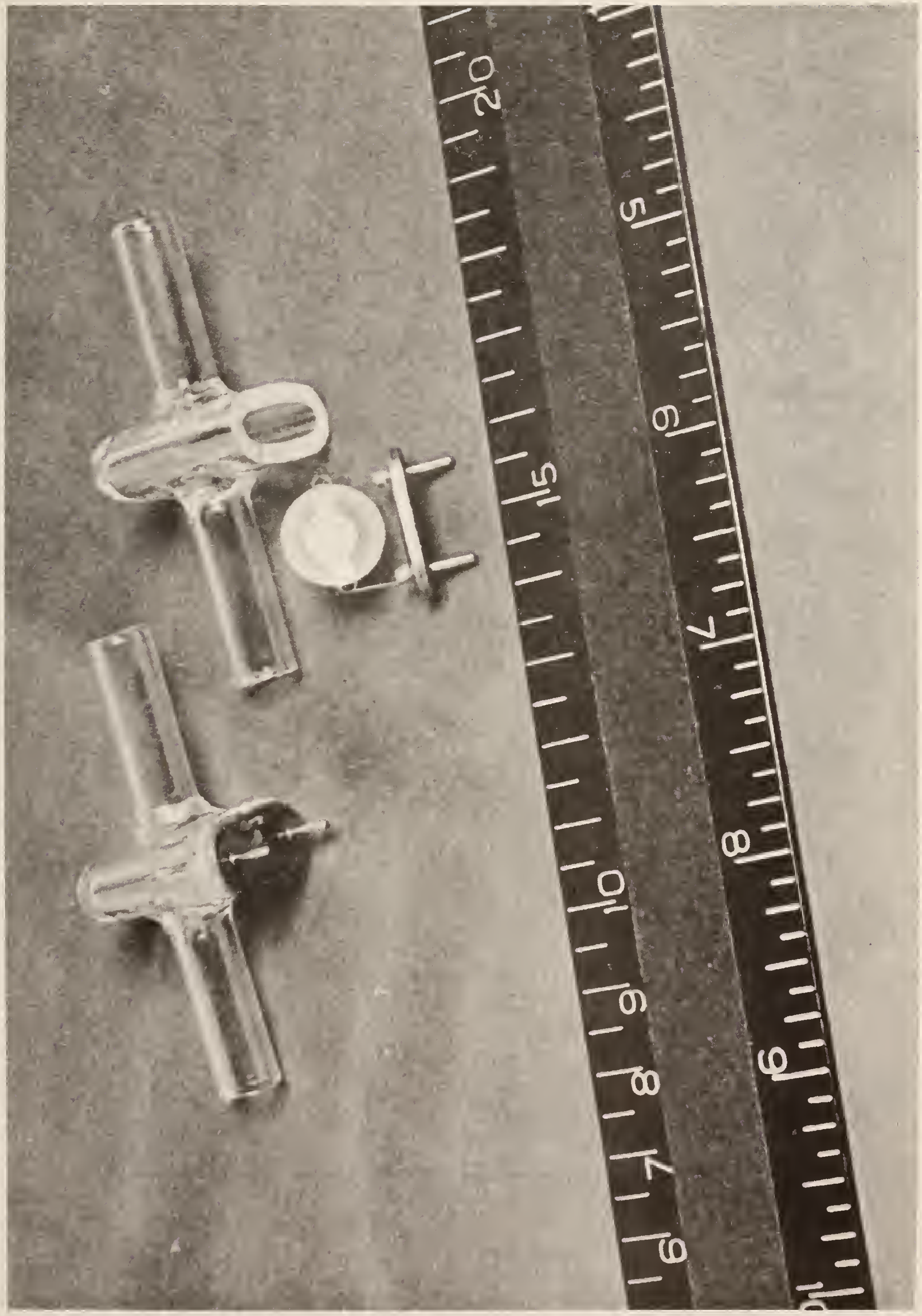


Figure 17.1 Piezoelectric crystal and glass holder into which it is sealed

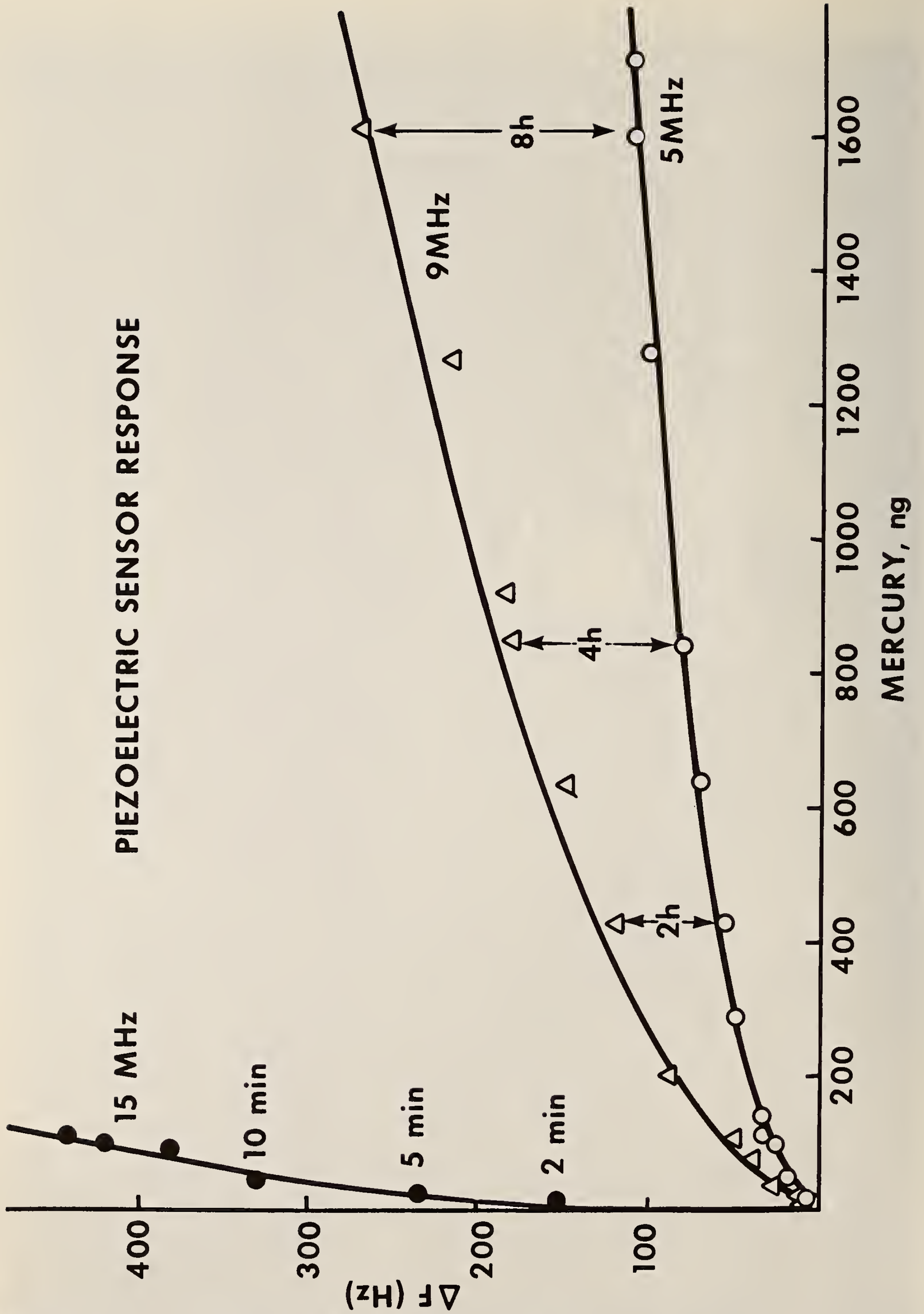


Figure 17.2 Response from sampling mercury vapor of 50 ng/l concentration.

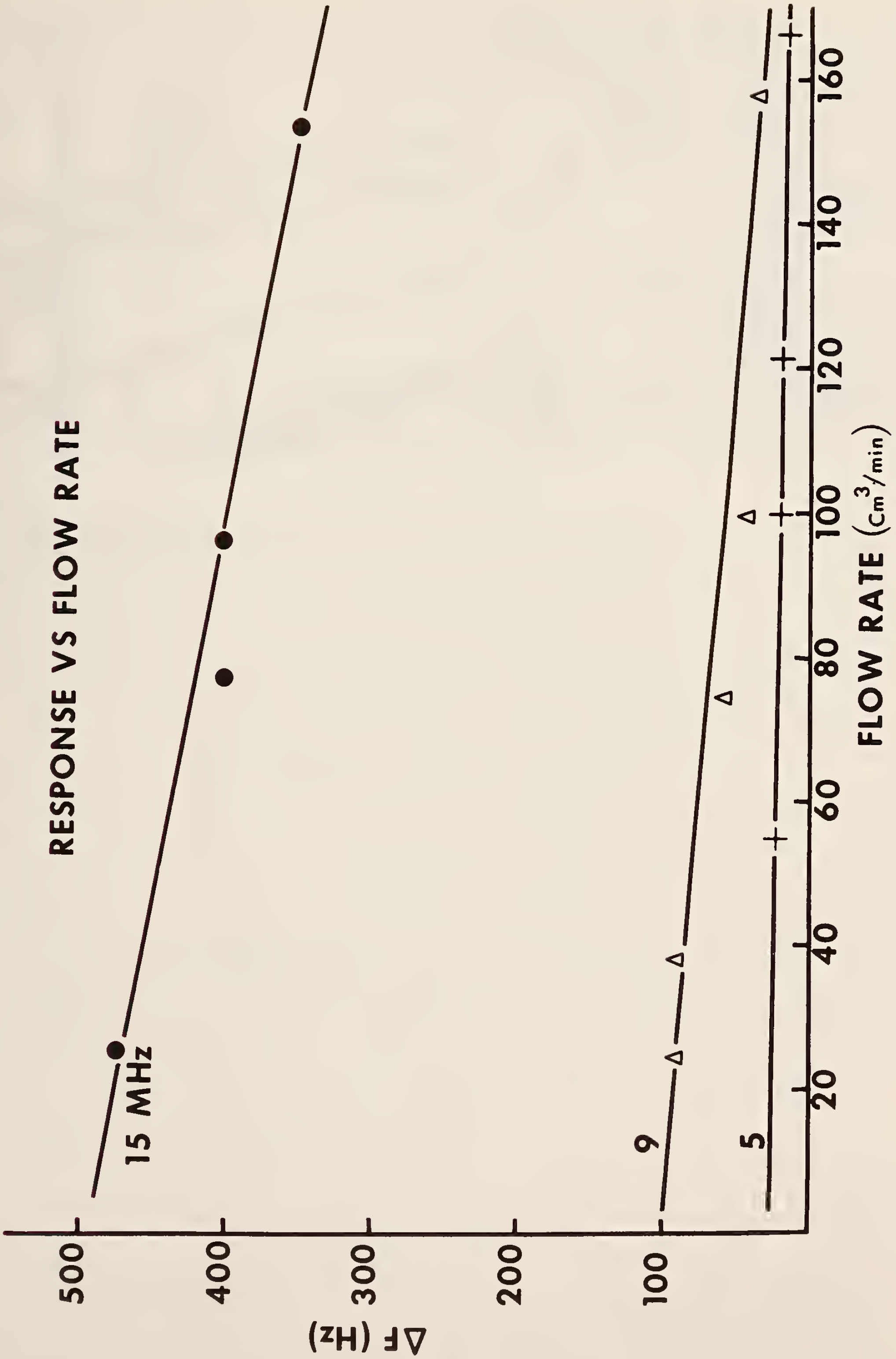


Figure 17.3 Sensor response vs. flowrate.

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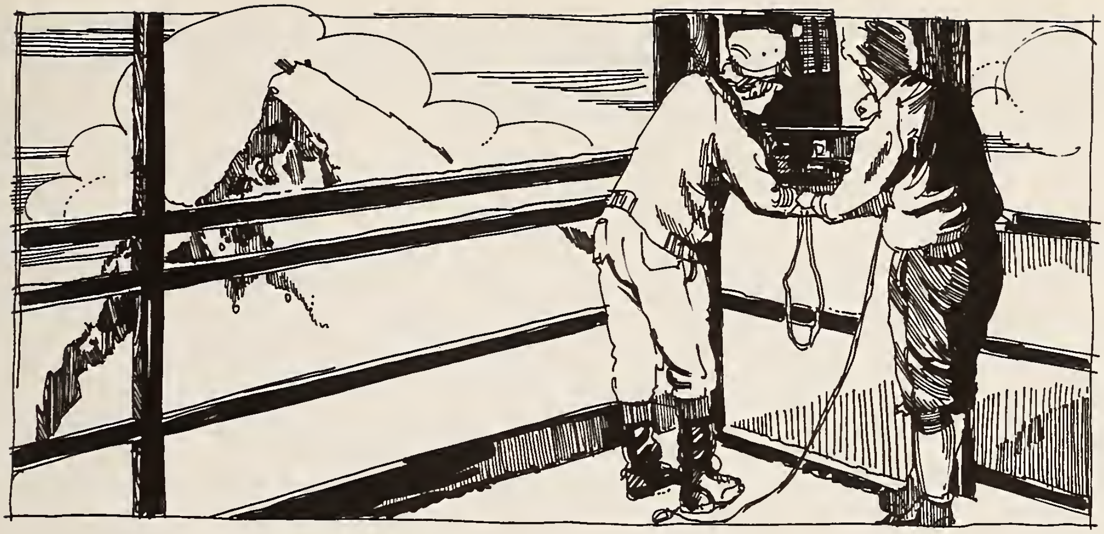

18. Measurement of Atmospheric ^{37}Ar by Isotopic Enrichment and Pulse Shape Discrimination Spectroscopy

Project Leader: L. A. Currie, Analytical Chemistry Division

Other Personnel: R. M. Lindstom (Anal. Chem. Div.), in collaboration with H. H. Loosli (Univ. Bern), L. Machta (NOAA), W. Roos (Mound Laboratories), J. Barkley (NBS) and P. Shoenfeld (NBS)

Objective

Argon-37 is produced naturally through the interaction of cosmic rays with atmospheric argon, with a pronounced vertical profile. As its half-life (35.1 days) is relatively short and because it is chemically so unreactive it represents an ideal tracer for the measurement of atmospheric mixing. Complications arising from processes such as rainout, fallout, chemical reaction, and exchange among reservoirs are completely avoided.

The quantitative connection between cosmic ray production and atmospheric concentrations of ^{37}Ar, and stratospheric and tropospheric mixing processes, has been clearly set forth in the steady-state model of Machta[1]. A principal result of the model is that, given the absolute production profile of ^{37}Ar in the atmosphere, one can derive important information about tropospheric mixing from the determination of the ground-level concentration of the nuclide.

The temporary contamination of the Northern Hemisphere with substantial amounts of noncosmic ^{37}Ar necessitated concentration on efforts at measurement of samples from the Southern Hemisphere, with which there would be insignificant mixing within the mean lifetime of the isotope.

Progress

The system for reliable sampling and sensitive measurement of atmospheric ^{37}Ar has been set up at NBS. Isotopic separation prior to counting was carried out at the Mound Laboratories[2] in an 11 column thermal diffusion cascade, with an effective length of over 37 meters. An enrichment factor of 70 or greater could be readily obtained. Feedstock gas could be either argon from air reduction plants, or a concentrated atmospheric sample purified over CaC_2 to remove the balance of non-noble gases.

Low level counting was carried out using the unique NBS system[3] which enables a great reduction in background via pulse risetime discrimination. This allowed the measurement of trace concentrations of ^{37}Ar in reasonable counting time periods, which would not otherwise have been possible. Delrin and brass counters of conventional design were utilized for the bulk of the present work.

Results were obtained for several samples from the Southern Hemisphere, along with preliminary data on a number of samples from various localities, including stratospheric gases. Interlaboratory comparisons with the Universitat Bern demonstrated the precision of the measurements. These results demonstrated the utility of the technique for the determination of tropospheric mixing. It was also found that significant ^{37}Ar contamination persisted even in these measurements, presumably due to nuclear testing in the South Pacific region. Later samples from Brazil, Argentina and Australia (Spring 1974) were free of contamination, and provided valuable data on mixing processes[4].

In order to define the vertical production gradient for ^{37}Ar, samples of dead material were exposed to high altitude conditions for extended periods. This was carried out at the Jungfraujoch and the Signalkuppe, two tall Swiss mountain peaks with relative atmospheric depths, at the point of exposure, of 560 and 670 gm/cm^2, respectively. Combined with the model of Lal and Peters[5], these data allowed precise determination of the altitude gradient.

To complete the study cross sections for the reaction Ar(p,x) ^{37}Ar were determined. This is the primary mode of production of natural ^{37}Ar. The values are, in millibarns, (at 50 MeV) 4.4, (at 92 MeV) 8.6, and (at 200 MeV) 13.2. In addition cross sections for the Ar (p,x) reaction to yield other nuclides, namely ^{39}Cl, ^{38}Cl, ^{34}Cl, ^{38}S and ^{31}S, were measured[4].

Further data and interpretation are forthcoming in the final report for this project.

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19. Origin of Atmospheric Hydrocarbons

Project Leader: L. A. Currie, Analytical Chemistry Division
Other Personnel: D. Breiter, E. Wolle, B. Andrews

Approach

Atmospheric hydrocarbons in urban areas have frequently been assumed to arise as a consequence of automobile or industrial pollution. However a major question has been raised recently as to the relative contributions of Nature versus Man. Various allegations (and measurements) have been made suggesting that the major contribution at least in the eastern cities may arise from natural sources, such as forests[1]. On a global scale this addition to the hydrocarbon reservoir is over seven times that of man.

The elucidation of these relative effects has an obvious impact upon pollution control and energy resource utilization. We are preparing to measure the origin of individual species present in atmospheric samples by examining their radiocarbon content. All man made contributions of significance to atmospheric hydrocarbons above methane are derived from petroleum, which is devoid of radiocarbon as a result of its geological age. It is therefore possible to determine the various sources of tropospheric pollutants by analyzing air samples by gas chromatography and, after combustion and conversion of the desired compound, counting the resultant gas in a properly designed proportional counter.

Progress

We have adapted our existing low level counting system for the measurement of small samples (less than 100 milliliters) of carbon dioxide and/or methane. This corresponds to 10-20 milligrams of carbon per counter fill. Several new quartz and copper microcounters of very low background and high efficiency have been fabricated toward this goal. We have, in addition, more conventional 1 and 1.5 liter counters which may prove useful for calibration studies. Background rates for the entire system are generally in the range of 0.17 cpm. A filling system particularly adapted to the small counters has also been constructed.

The relative merits of methane and carbon dioxide as counting gases have been evaluated, and the results compared with gases of known efficiency. We find methane to be preferable from the standpoint of signal/noise and resolution of the pulse energy-pulse risetime profile. Carbon dioxide will perform satisfactorily but at a slightly increased noise level [2].

The problem of sample purity is especially acute in the present system due to the fast pulse risetime which is required from the counter in order to collect meaningful data. We have therefore undertaken a study of the effect of trace impurities upon the counting process. It has been found that conventionally purified carbon dioxide such as is used in most radiocarbon laboratories is of insufficient purity for our purposes. In addition to devising a further purification scheme we have to some extent improved this difficulty by increasing the time constant of the counter guard circuit so as to provide coincident pulse blanking throughout the irregular risetime of the data pulse.

A number of preliminary studies have been carried out upon radiocarbon calibration standards and other materials of interest. Working standard carbon dioxide from F. J. Pearson (USGS-Reston) and E. Ralph (Univ. of Pennsylvania) have been measured in both the small and large counters. Standard deviations and non-Poisson random error have been computed in each case. Preliminary data on a sample of urban particulate containing 12% carbon indicate an upper limit of 20% of contemporary levels, demonstrating the utility of the approach to such samples. These data compare favorable with that of Clayton, Arnold, and Patty[3] on similar samples. Further refinement of the sample is continuing.

We have considered various atmospheric sampling techniques, and have decided, in addition to particulates, to confine most of our efforts toward selective adsorption of the hydrocarbons upon cryopumped molecular sieves. Currently we are constructing a high purity microcombustion line and conversion apparatus which can be interfaced directly with a flame ionization analytical gas chromatograph. This arrangement will allow the rapid processing of trace compounds in large volume air samples.

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20. Lead in Gasoline

Project Leader: I. L. Barnes, Analytical Chemistry Division
Other Personnel: N. M. Caliman, J. W. Gramlich, E. F. Heald, and T. J. Murphy

Objective

To develop a method for the accurate determination of lead in gasoline and reference fuels by isotope dilution mass spectrometry.

Approach

The conditions for the quantitative conversion of the organically bound lead in gasoline and reference fuels to inorganic lead were to be established. Lead could then be accurately determined by spiking with 206 separated isotope of lead and mass spectrometric analysis.

Progress

A method has been developed for the accurate determination of lead in gasoline. It has been used to certify the lead concentration in Standard Reference Materials, SRM's 1636, 1637, and 1638, Lead in Reference Fuels. These SRM's consist of four separate blends of leaded fuel which vary in concentration from 12 to 773 µg Pb/g. The method has also been used to determine the lead concentration in the Gasoline Fossil Fuel Standard.

The success of the method depends on the quantitative conversion of the organically bound lead of the fuel to inorganic lead. After experimenting with several methods, the following method was found to give quantitative conversion without loss of volatile lead compounds.

A sample of the fuel (about 1g) is transferred to a Pyrex Erlenmeyer flask containing 5 ml[1] of concentrated nitric acid and ^{206}Pb spike. The flask is stoppered with a polyethylene stopper and the contents are rapidly stirred using magnetic stirring for one hour. The flask and contents are then shaken for five minutes to ensure reaction with any volatile lead. For hydrocarbon reference fuels, the mixture is simply evaporated to dryness. For gasoline, 1 ml of perchloric acid is added and the solution is evaporated to fumes of perchloric acid.

[1] The abbreviation ml, for milliliter is used in this publication. The new abbreviation for milliliter is mL.

At this point, the lead is available for separation and determination by mass spectrometry (or other techniques).

The results of the determination of lead in the Gasoline Fossil Fuel Standard and the SRM Reference Fuels are shown in tables 20.1 through 20.5.

The analysis of the Gasoline Standard, Table 20.1, shows that one bottle. 564, had a lead concentration two percent higher than the other four bottles. This could be due to loss of gasoline and concentration of tetra-ethyl lead. The results for the other bottles show that the material contained 375.0 ± 2.2 μg Pb/g. The results for bottle 141 show that no lead is lost during the equilibration-oxidation steps since there is no significant difference between the results for sub-samples 1 and 2 which were spiked before the analysis and sub-samples 3 and 4 which were spiked after the evaporation of HNO_3.

The SRM Reference Fuels have been certified on the basis of the results reported in table 20.2 through 20.5 as follows:

Nominal Lead Concentration g/gal	Certified Lead Concentration μg/g
0.03	12.31 ± 0.06
0.05	19.68 ± 0.05
0.07	27.70 ± 0.06
2.00	772.70 ± 1.50

The uncertainties cited represent the pooled 95% confidence interval for a single determination with allowance for known sources of possible error.

An investigation of the concentration and type of acid used for the conversion of the organically bound lead was also completed. The results are shown in Tables 20.6 and 20.7. They show that quantitative results were obtained only when concentrated nitric acid was used. Low recoveries were found for hydrochloric acid and more dilute nitric acid concentrations.

Table 20.1 Lead in Gasoline Fossil Fuel Standard.

Bottle No.	Sample No.	Lead µg/g	
141	1	375.1	
	2	375.0	
	3[a]	376.6	
	4[a]	376.8	
	Average		375.9
226	1	374.9	
	2	375.2	
	Average		375.0
323	1	373.4	
	2	375.1	
	Average		374.3
564	1	380.5	
	2	384.5	
	Average		382.5
707	1	374.3	
	2	374.8	
	Average		374.6
	Grand Average (Bottle 564 omitted)		375.0 ±2.2[b]
	Grand Average (Bottle 564 included)		376.5 ±6.9[b]

---

[a] Spiked after evaporation of HNO_3.

[b] 95% L.E. for Single Analysis.

Table 20.2 Lead in Reference Fuel 2.0 g Lead/Gallon Standard.

			Lead μg/g
Can A			
Vial	5		772.4
	319		772.1
	735		773.6
		Average	772.7 ± 1.5[a]
Can B			
Vial	995		745.8[b]
	1078		742.1
Bulk	1		742.5
	2		740.8
	3		741.6
	4		741.4
		Average	741.6 ± 1.5[a]

---

[a] Pooled 95% confidence limit for an individual determination.

[b] Excluded from average (sample taken one hour after opening vial.)

Table 20.3 Lead in Reference Fuel 0.07 g Lead/Gallon Standard.

Vial		Lead µg/g
95		27.70
212		27.71
444		27.70
494		27.69
645		27.75
823		27.68
825		28.23[a]
828		27.70
828		27.69
1019		27.69
1155		27.73
	Average	27.70 ± 0.06[b]
EPA (first series)		
8		27.64
61		27.65
128		27.78
	Average	27.69
EPA (second series)		
Front		27.78
Middle		27.77
Rear		27.82
	Average	27.79

---

[a] Excluded from average

[b] 95% confidence limit for an individual determination.

Table 20.4 Lead in Reference Fuel 0.05 g Lead/Gallon Standard.

		Lead µg/g
Can A		
Vial 31		19.67
71		19.70
637		19.68
	Average	19.68 ± 0.05[a]
Can B		
Vial 970		19.81
1140		19.86
Bulk 1		19.85
2		19.87
3		19.87
4		19.83
	Average	19.85 ± 0.05[a]
EPA (first series)		
Vial 35		19.61
85		19.76
120		19.88
	Average	19.75
EPA (second series)		
Dial Front		19.83
Middle		19.82
Rear		19.80
	Average	19.82

---

[a] Pooled 95% confidence limit for an individual determination.

Table 20.5 Lead in Reference Fuel 0.03 g Lead/Gallon Standard.

Vial		Lead µg/g
138		12.32
285		12.30
352		12.29
506		12.33
633		12.36
812		12.30
911		12.30
1061		12.28
	Average	12.31 ± 0.06[a]
EPA (first series)		
2		12.40
54		12.37
1301		12.34
	Average	12.37
EPA (second series)		
Front		12.33
Middle		12.32
Rear		12.32
	Average	12.32

---

[a] 95% confidence limit for an individual determination.

Table 20.6 Effect of Nitric Acid Concentration on Recovery of Lead in Gasoline.

Sample No.	HNO_3 N[a]	Lead Found ppm	Recovery[b] %
1	16	376.6	100.4
2	16	372.9	99.4
3	16	376.3	100.3
4	16	378.1	100.8
5	8	376.5	98.0
6	8	369.7	98.6
7	4	346.8	92.5
8	4	352.3	93.9
9	2	141.3	37.7

---

[a] Concentration of the 5 ml of added acid.

[b] Based on previous analysis of 375.0 ± 2.2 ppm Pb.

Table 20.7 Effect of Hydrochloric Acid Concentration on Recovery of Lead in Gasoline.

Sample No.	HCl N[a]	Lead Found (ppm)	Recovery[b]
1	10	367.5	98.0%
2	10	349.8	93.3%
3	10	352.9	94.1%
4	10	267.7	71.3%
5[c]	10	370.6	98.8%
6[c]	10	246.5	65.7%
7[c]	10	375.7	100.2%
8[c]	10	198.1	52.8%
9	5	319.0	85.1%
10	5	249.2	66.5%
11	1	16.1	4.3%
12	1	48.5	12.9%
13	0.2	11.8	3.1%
14	0.2	16.8	5.0%

---

[a] Concentration of the 5 ml of added acid.

[b] Based on previous analysis of 375.0 ±2.2 ppm.

[c] Spiked after evaporation.

21. Degradation of Polymers

Project Leader: R. E. Florin, Polymers Division
Other Personnel: J. H. Flynn, S. Straus, L. Dunlap, W. J. Pummer

Objective

To gain an understanding of the mechanisms of polymer degradation, primarily thermal decomposition to volatiles. Applications are to limits on service, fire hazard, incineration, and toxic hazard.

Approach

Data for the deduction of mechanism are pyrolysis rates and molecular weights as a function of conversion. Products are characterized also for newly studied polymers. Interpretation is in terms of the free radical chain theory. Burning of aged polymers is also studied.

Progress

Experimental work was completed upon the pyrolysis of polyoctafluorostyrene fractions of various molecular weights. Monomer is not an important product, a fact which raises difficulties as to the type of reaction that can produce oligomer fractions in an all-fluorocarbon polymer. Data from the pyrolysis of azobis-isobutyronitrile prepared polystyrene showed very high initial rates for some low-molecular-weight fractions, which are not yet satisfactorily explained, although they correlated with several anomalous pyrolysis gas chromatography peaks. The pyrolysis of polystyrene in nitrogen showed rate versus conversion curves similar to vacuum experiments but apparently about 30% higher not lower. Before drawing conclusions, a careful check is being made of temperature distributions under the two conditions. Burning behavior and extent of oxidation were studied for four polymers aged in air by the action of heat and also by gamma rays. Appreciable effects were: for polypropylene oxidized under gamma rays, an appreciable increase in ignition time; and, for flexible polyurethane aged in an oven, an increase in burning rate.

22. Fossil Fuel Standards

Project Leader: P. D. LaFleur and D. A. Becker, Analytical Chemistry Division
Other Personnel: Many scientists throughout the Analytical Chemistry Division

Objective

To develop environmental trace element standards for fossil fuel energy requirements.

Approach

The approach that has been used was to obtain samples of the required materials for processing and issuance as Standard Reference Materials. This processing included insuring the material had a limited particle size range, proving homogeneity on the final bottled sample, and finally analyzing and certifying these materials for trace element content. A much more detailed description of the materials and the processing required for each of them is contained in last year's Measures for Air Quality Annual Report, NBS Technical Note 828.

Progress

The Trace Elements in Fly Ash (SRM 1633), Trace Elements in Coal (SRM 1632), and Trace Elements in Residual Fuel Oil (SRM 1634) have been issued--see certificates for details.

The Trace Elements in Gasoline SRM has presented a number of significant technical problems and because of this has been dropped as a candidate SRM.

The gasoline was analyzed for its lead content by isotope dilution mass spectrometry, which revealed that with leaded gasoline, the problem of volatility is extremely significant. This is compounded by the fact that the tetra-ethyl lead apparently has a different volatility than the gasoline hydrocarbon component. In addition to the above problem, there has been great difficulty in the attempts to process the gasoline into a form suitable for analysis by conventional analytical techniques. In this case the problems include both volatility, and the potential for rapid, uncontrolled oxidation. The volatility problem is especially difficult to evaluate because it is not known which of the trace element components are in metallo-organic form and what their individual vapor pressures are in relation to the hydrocarbon component of the gasoline. These problems have resulted in the decision that gasoline is an inappropriate material for a trace element standard.

U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards
Certificate of Analysis

Standard Reference Material 1632

Trace Elements in Coal

This Standard Reference Material is intended for use in the calibration of apparatus and methods used in analyses of coals and other materials with similar matrices for trace elements. This material should be dried without heat to a constant weight before using. Recommended procedures for drying are: (1) drying for 24 hours using a cold trap at or below −50 °C and a pressure not greater than 30 Pa (0.2 mm Hg); (2) drying in a desiccator over P_2O_5 or $Mg(ClO_4)_2$. When not in use, the material should be kept in a tightly sealed bottle and stored in a cool, dark place. Long term (> 1 year) stability of this SRM has not been rigorously established. NBS will continue to monitor this material and any substantive change will be reported to purchasers.

The certified values given below are based on at least a 250-mg sample of the dried material, the minimum amount that should be used for analysis.

Element[1]	Content[2] µg/g	Element[1]	Content[2] µg/g
Iron[g,i]	8700 ± 300	Selenium[d,e]	2.9 ± 0.3
Manganese[a,e]	40 ± 3	Uranium[c,f]	1.4 ± 0.1
Zinc[d,e]	37 ± 4	Thallium[c,d]	0.59 ± 0.03
Vanadium[b,e,g]	35 ± 3	Cadmium[d,e,i]	0.19 ± 0.03
Lead[a,c,i,d]	30 ± 9	Mercury[a,e,]	0.12 ± 0.02
Chromium[a,c,e]	20.2 ± 0.5		
Copper[a,d,g]	18 ± 2		
Nickel[c,g,i]	15 ± 1		
Arsenic[e,h]	5.9 ± 0.6		

1. Methods of Analyses:
   - a. Atomic Absorption Spectrophotometry
   - b. Flame Emission Spectrometry
   - c. Isotope Dilution Mass Spectrometry
   - d. Isotope Dilution Spark Source Mass Spectrometry
   - e. Neutron Activation
   - f. Nuclear Track Technique
   - g. Photometric
   - h. Photon Activation
   - i. Polarography
2. The values are based on the results of 4 to 17 determinations by each of at least two analytical techniques. The estimated uncertainties include sample variations, possible method differences, and errors of measurement (but in no case less than the 95% confidence limits computed for the analyses).

The overall direction and coordination of the analytical measurements leading to this certificate were performed in the Analytical Chemistry Division under the chairmanship of P. D. LaFleur.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by C. L. Stanley.

Washington, D. C. 20234
March 7, 1975

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

PREPARATION, TESTING, and ANALYSIS

This material is a blend of commercially available coals supplied by five electric power plants: Tennessee Valley Authority, Stevenson, Alabama; Commonwealth Edison, Chicago, Illinois; Baltimore Gas and Electric Co., Baltimore, Maryland; Carolina Light and Power Co., Roxboro, North Carolina; and Potomac Electric Power Co., Washington, D. C. These plants were specially selected to provide coals that covered a broad spectrum of the coal mining industry. Some of the coals required regrinding to obtain a fine particle size. This was done under the auspices of Mr. Forrest Walker of the U. S. Bureau of Mines, Pittsburgh, Pennsylvania. The coals were then sieved and the portion passing through a 120 mesh sieve and retained on a 325 mesh sieve was taken (125 to 44 micrometers diameter). After sieving, the five coals were blended in a double-coned blender. After 1 hour the material was immediately removed and bottled.

A random scheme for sample selection was designed and a statistical analysis of the homogeneity data was performed by J. Mandel of the NBS Institute for Materials Research. Thirteen of 500 bottles were selected for homogeneity tests. These samples were analyzed for aluminum and manganese by nondestructive neutron activation analysis. Replicate analyses on 250-mg samples indicated homogeneity within ±5 (relative) based on these two elements. The homogeneity analyses were performed in the NBS Analytical Chemistry Division by T. E. Gills and S. H. Harrison. Analyses for the various elements were made in the NBS Analytical Chemistry Division by the following analysts: R. K. Bell, R. W. Burke, B. S. Carpenter, B. I. Diamondstone, L. P. Dunstan, M. S. Epstein, E. L. Garner, T. E. Gills, E. S. Gladney, J. W. Gramlich, G. J. Lutz, L. A. Machlan, E. J. Maienthal, L. T. McClendon, T. J. Murphy, E. Orvini, P. J. Paulsen, T. C. Rains, K. M. Sappenfield, S. A. Wicks.

The following values are not certified because they are based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

Element	Content (μg/g)
Titanium	(800)
Cobalt	(6)
Silicon	(3.2%)
Thorium	(3.0)
Beryllium	(1.5)
Silver	(≤0.1)
Tellurium	(<0.1)

U. S. Department of Commerce
Rogers C. B. Morton
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards
Certificate of Analysis
Standard Reference Material 1634
Trace Elements in Fuel Oil

This Standard Reference Material is intended for use in the calibration of apparatus and evaluation of methods used in analyses of fuel oil and other materials with similar matrices for trace elements. When not in use, the material should be kept in a tightly sealed bottle. Long term (>1 year) stability of this SRM has not been rigorously established. NBS will continue to monitor this material and any substantive change will be reported to purchasers.

The certified values given below are based on at least a 250-mg sample of the material, the minimum amount that should be used for analysis.

Element	Content[2]		μg/g except S in % by weight
Sulfur[d,e]	2.14	±	0.02%
Nickel[a,b,g]	36	±	4
Lead[b,g]	0.041	±	0.005
Vanadium[a,d]	320	±	15
Zinc[d,g]	0.23	±	0.05
Iron[a,d,g]	13.5	±	1.0

1. Methods of Analyses:
   - a. Atomic Absorption Spectrophotometry
   - b. Isotope Dilution Mass Spectrometry
   - c. Isotope Dilution Spark Source Mass Spectrometry
   - d. Neutron Activation
   - e. Combustion with Titrimetry
   - f. Spectrophotometry
   - g. Polarography
2. The values are based on the results of 4 to 15 determinations by each of at least two analytical techniques. The estimated uncertainties include sample variations, possible method differences, and errors of measurement (but in no case less than the 95% confidence limits computed for the analyses).

The overall direction and coordination of the analytical measurements leading to certification were performed in the Analytical Chemistry Division under the chairmanship of P. D. LaFleur and D. A. Becker.

(over)

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by C. L. Stanley.

Washington, D. C. 20234 J. Paul Cali, Chief
May 14, 1975 Office of Standard Reference Materials

PREPARATION, TESTING, and ANALYSIS

The material was obtained through a commercial supplier from a refinery on the island of Aruba in the West Indies, and is essentially a "No. 6 Fuel Oil" as defined by the American Society for Testing and Materials.

A random scheme for sample selection was designed and a statistical analysis of the homogeneity data was performed by J. Mandel of the NBS Institute for Materials Research. Fifteen of 500 bottles were selected for homogeneity tests. These samples were analyzed for vanadium by nondestructive neutron activation analysis. Replicate analyses on 250 mg samples indicated homogeneity within ±2% (relative) based upon this element. X-ray fluorescence analyses for sulfur on bulk samples before bottling supports the conclusion of acceptable material homogeneity. The homogeneity analyses were performed in the NBS Analytical Chemistry Division by T. E. Gills, M. Darr, and R. Myklebust. Analyses for the various elements were made in the NBS Analytical Chemistry Division by the following analysts: R. W. Burke, B. S. Carpenter, M. S. Epstein, E. L. Garner, T. E. Gills, J. W. Gramlich, L. A. Machlan, E. J. Maienthal, T. J. Murphy, E. Orvini, T. C. Rains, H. L. Rook, T. A. Rush, and S. A. Wicks.

The following values are not certified because they are based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

Element[1]	Content µg/g
Arsenic[d]	(0.095)
Beryllium[f]	(<0.01)
Cadmium[d,g]	(<0.01)
Chromium[d]	(0.09)
Mercury[d]	(0.0023)
Manganese[d]	(0.12)

U. S. Department of Commerce
Frederick B. Dent
Secretary
National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards
Certificate of Analysis
Standard Reference Material 1633
Trace Elements in Coal Fly Ash

This Standard Reference Material is intended for use in the calibration of apparatus and methods used in analyses of coal fly ash and other materials with similar matrices for trace elements. This material should be dried to a constant weight before using. Recommended procedures for drying are: (1) drying for 24 hours using a cold trap at or below −50 °C and a pressure not greater than 30 Pa (0.2 mm Hg); (2) drying in a desiccator over P_2O_5 or $Mg(ClO_4)_2$. When not in use, the material should be kept in a tightly sealed bottle. Long term (>1 year) stability of this SRM has not been rigorously established. NBS will continue to monitor this material and any substantive change will be reported to purchasers.

The certified values given below are based on at least a 250-mg sample of the dried material, the minimum amount that should be used for analysis.

Element[1]	Content[2] μg/g	Element[1]	Content[2] μg/g
Manganese^{a,e,g}	493 ± 7	Nickel^{a,c,i}	98 ± 3
Zinc^{a,e}	210 ± 20	Arsenic^{e,h}	61 ± 6
Vanadium^{b,e,g}	214 ± 8	Uranium^{e,f}	11.6 ± 0.2
Lead^{c,i}	70 ± 4	Selenium^{d,e}	9.4 ± 0.5
Chromium^{a,c,e,i}	131 ± 2	Cadmium^{a,d,i,e}	1.45 ± 0.06
Copper^{a,d,j}	128 ± 5	Mercury^{a,e}	0.14 ± 0.01

1. Methods of Analyses:
    - a. Atomic Absorption Spectrophotometry
    - b. Flame Emission Spectrometry
    - c. Isotopc Dilution Mass Spectrometry
    - d. Isotope Dilution Spark Source Mass Spectrometry
    - e. Neutron Activation
    - f. Nuclear Track Technique
    - g. Photometric
    - h. Photon Activation
    - i. Polarography
    - j. Colorimetry
2. The values are based on the results of 4 to 28 determinations by each of at least two analytical techniques. The estimated uncertainties include sample variations, possible method differences, and errors of measurement (but in no case less than the 95% confidence limits computed for the analyses).

The overall direction and coordination of the analytical measurements leading to certification were performed in the Analytical Chemistry Division under the chairmanship of P. D. LaFleur.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by C. L. Stanley.

Washington, D. C. 20234
March 7, 1975

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

PREPARATION, TESTING, and ANALYSIS

This material is a blend of coal fly ashes supplied by five electric power plants: Tennessee Valley Authority, Stevenson, Alabama; Commonwealth Edison, Chicago, Illinois; Baltimore Gas and Electric Co., Baltimore, Maryland; Carolina Light and Power Co., Roxboro, North Carolina; and Potomac Electric Power Co., Washington, D. C. These plants were specially selected to provide fly ashes that covered a broad spectrum of the fly ashes from the coal mining industry. Five of the fly ashes were collected by electrostactic precipitators and one by a mechanical collector. The fly ashes were sieved and the portion passing through a 170 mesh sieve was taken (88 micrometers diameter or less). After sieving, the fly ashes were blended in a double-coned blender. After 1 hour the material was immediately removed and bottled.

A random scheme for sample selection was designed and a statistical analysis of the homogeneity data was performed by J. Mandel of the NBS Institute for Materials Research. Fifteen of 500 bottles were selected for homogeneity tests. These samples were analyzed for manganese by nondestructive neutron activation analysis. Replicate analyses on 250 mg samples indicated homogeneity within ±5% (relative) based upon this element. X-ray fluorescence analyses on bulk samples before bottling supports this conclusion with values for calcium, titanium, iron, nickel, zinc, strontium, and barium. The homogeneity analyses were performed in the NBS Analytical Chemistry Division by T. E. Gills and S. D. Rasberry. Analyses for the various elements were made in the NBS Analytical Chemistry Division by the following analyst: R. K. Bell, B. S. Carpenter, L. P. Dunstan, M. S. Epstein, E. L. Garner, T. E. Gills, E. S. Gladney, J. W. Gramlich, G. J. Lutz, L. A. Machlan, E. J. Maienthal, L. T. McClendon, T. J. Murphy, E. Orvini, P. J. Paulsen, T. C. Rains, T. A. Rush, and K. M. Sappenfield.

The following values are not certified because they are based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

Element	Content (μg/g)
Potassium	(1.72%)
Strontium	(1380)
Rubidium	(112)
Cobalt	(38)
Thorium	(24)
Beryllium	(12)
Thallium	(4)

23. Determination of Platinum and Palladium by Activation Analysis

Project Leader: D. A. Becker, Analytical Chemistry Division

Objective

The objective of this project is to develop an accurate and precise trace element analytical technique for the determination of platinum and palladium in biological and environmental materials.

Approach

The utilization of vehicular exhaust catalytic converters containing these noble metals underscores the need for accurate and sensitive analytical techniques for the noble metals in the environment, especially for platinum and palladium [1-3]. Neutron activation analysis is able to analyze both of these elements at the μg/g concentration level or below. Earlier work in this laboratory has established that platinum can be determined at the .01 μg/g concentration level in glasses. However, in order to determine these elements at the trace level they must be chemically separated from the matrix material after irradiation. This is necessary due to their low energy gamma rays which are used for analysis. This effort has therefore been towards development of a radiochemical separation technique that will allow the determination of platinum and palladium accurately and reliably at the μg/g to ng/g concentration levels in a wide variety of environmental materials.

Progress

The neutron activation analysis method developed and described here is capable of quantitatively determining gold, platinum and palladium in a wide variety of biological and environmental matrices. The nuclear characteristics of the radioisotopes used in this procedure are found in Table 23.1. As shown, the isotope used for the determination of platinum is the gold-199 daughter from platinum-199.

In addition to the matrices described here, this method is currently being applied also to the analysis of several new biological standard materials currently undergoing certification, a fresh water sediment being evaluated as a potential reference material, and an urban air particulate material.

All samples were prepared for analysis by lyophilization. Dry samples weighing from twenty to two-hundred milligrams each were placed into precleaned, polyethylene snap cap vials for neutron irradiation. The facility used was the NBS nuclear reactor, with irradiation periods of up to four hours at a thermal neutron flux of 5.6×10^{13} $n \cdot cm^{-2}$ s^{-1}.

The chemical separation technique employed involved wet-ashing the irradiated biological or environmental sample with approximately ten milliliters of a three to one mixture of concentrated nitric and perchloric acids. This sample dissolution took place in the presence of about one milligram each of platinum, gold and palladium carriers, and about five milligrams of copper holdback carrier. The samples were slowly wet-ashed on a hot plate to fumes of perchloric acid, then taken almost to dryness. After cooling, they were taken up in about three milliliters of a three to one mixture of concentrated hydrochloric and nitric acids until complete dissolution occurs. An additional five milligrams of copper holdback carrier was added at this time, along with several milligrams of scandium and phosphate holdback carriers. Samples were then diluted to approximately twenty milliliters, and quantitatively transferred into appropriately sized disposable plastic containters (e.g., centrifuge tubes, bottles, etc.). At this point, 200 milligrams of finely divided silver metal powder was added, and the solution-powder mixture stirred for approximately five minutes using a magnetic stirring bar with high agitation. The silver powder should swirl throughout the entire solution during this period.

After spontaneous deposition onto the silver powder is concluded, the solution with silver powder is quantitatively transferred to a standard radiochemical filter chimney with a filter capable of retaining fine particle size material. In this work, glass fiber filter pads were used. The silver powder is washed several times with distilled water, and great effort is taken to ensure that all of the silver particles have been transferred to the filter. At this point, the silver powder on the filter paper is removed from the filter chimney and carefully transferred to a plastic disposable petri dish and mounted for subsequent counting. Separation of the silver by centrifugation was also investigated, but filtration was found to be more effective in removing the silver powder fines from the solution.

Aliquots of the dissolved standards are processed in exactly the same way in order to check radiochemical recovery. In addition, duplicate aliquots are added directly to filter paper in the disposable petri dishes producing a geometry similar to that of the processed sample.

Tracer studies made using this radiochemical separation procedure showed quantitative recovery (greater than 99.5%) for the gold-198, gold-199, and palladium-109.

This analytical system has been evaluated through application to the determination of gold, platinum, and palladium in several available biological and environmental materials. Results on the analysis of a bovine animal tissue (liver) gave values of 1.8 ng/g for gold, less than 1.6 ng/g for platinum, and less than 1 ng/g for palladium. Results for the analysis of a powdered botanical material (leaves) gave results of 0.2 ng/g for gold, less than 9 ng/g for platinum, and less than 1 ng/g for palladium. These analyses were made using a neutron flux of 5.6 x 10^{13} $n \cdot cm^{-2}\ s^{-1}$ for four hours, and counting both on a 6% efficient Ge(Li) detector (gold-198, gold-199) or LEPS System (109-palladium). For the botanical material, the less sensitive 208 keV gamma ray peak was used due to an interference with the 158 keV gamma ray. This interference was apparently due to the scandium-47 daughter from neutron irradiation of naturally stable calcium-47. Later determinations using scandium holdback carrier eliminated this interference problem.

In conclusion, the spontaneous deposition technique has been demonstrated for the first time to be an effective radiochemical separation method for biological and environmental samples, and neutron activation combined with this separation technique appears to be a very useful method for the determination of platinum, palladium, gold, and possibly other noble metals in biological and environmental materials.

Table 23.1 Radioisotopes Used for the Analyses of Neutron Activation

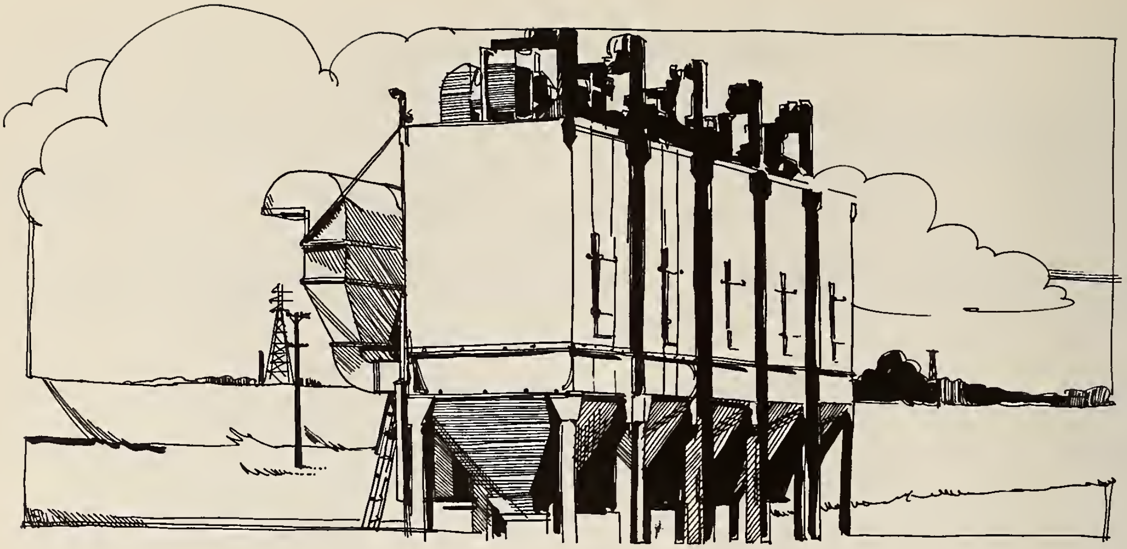
Element Determined	Radioisotope Used	Photon Energy	Half-Life
Gold	^{198}Au	412 keV	2.69 d
Platinum	^{199}Au (daughter)	158 keV (208 kev)	3.14 d
Palladium	^{109}Pd	88 keV	13.5 h

References

[1]. Kinard,W.D.,Becker,D.A., and LaFleur, P.D., *NBS Tech. Note 548* (1970) pp. 66-69.

[2]. Becker, D.A.,*Anal.Chem.Acta* 61, 1 (1972).

[3]. Park ,K.S., Gijbels,R., and Hoste, J., *Radioanal. Chem.* 5, 31 (1970).



24. Urban Dust Project

Project Leader: J. K. Taylor and W. Cassatt, Analytical Chemistry Division

Objective

To collect a large sample (25 kilograms) of urban air particulate from each of two metropolitan areas. One site is to be representative of highly industrialized communities while the other is to be typical of cities devoted to light commerce and residential developments. The samples will be characterized with respect to trace element composition, organic components, and particle size distribution.

Approach

Each of these samples will be homogenized separately and subdivided into several hundred samples for use as a Standard Reference Material. These SRMs will be issued by NBS to provide calibration and test materials for those involved in air particulate studies or air pollution monitoring. The reference materials will constitute known samples which have compositional and physical characteristics that are very similar to the material that the users are attempting to detect or analyze. Secondly, they will enable investigators to measure the sensitivities, matrix interferences and particle size effects that are associated with the particular instrument or analytical procedure that is being tested.

Progress

Five baghouses, each with an air sampling rate of approximately 6000 cubic feet of air per minute (163μm^3/min) were installed in December 1973 in the eastern section of the St. Louis metropolitan area (Granite City, IL). At the end of FY 74 (July 1974), the total dust mass collected in all the baghouses was about two kiligrams. This yield was particularly disappointing since it was estimated the total air particulates entering the bags was in the neighborhood of 27 kilograms.

During FY 75, the collection efficiency was observed to rise slowly as the mass of dust particles built up on the filter cloth. It was estimated from a few bats that had been weighed early in 1975 that approximately six kilograms had been collected by the end of January of that year. However, the average particulate collection efficiency for the entire period was still only nine percent.

In January 1975, a set of experiments was conducted in Washington, D. C., to determine whether the air velocity had any effect upon the collection efficiency of the cotton filter material. When a segment of a filter bag (which had been removed from baghouse No. 2) was placed in a Hi-Vol sampler with a fiberglass filter behind the cloth, it yielded a measured collection efficiency of 93 percent. The linear velocity through the cloth was ~20 times the velocity through the bags in the baghouses. The results indicate that the effect of flow rate on the baghouse efficiency warranted investigation.

Toward the end of January 1975 a Hi-Vol system was operated for 16 hours inside baghouse No. 5 in St. Louis and then was run outside the baghouse for an equal period of time. The Hi-Vol sampler collected 39 mg of dust inside unit 5 as compared to 145 mg outside. This gave an estimate of 70 percent for the baghouse collection efficiency. A repeat of this experiment in April yielded an efficiency reading of 90 percent.

Early in April 1975, ~90 percent of the bags from unit 5 and one bag from unit 4 were brought back to NBS. Weighing data on the dust that was vacuumed from four bags from unit 5 and one bag from unit 4 indicated that a total of about nine kilograms of material had been collected by all five baghouses up to that time (April 1975). Another sample taken from unit 4 at the end of May indicated that roughly 10 kilograms were contained in all units as of June 1975.

Seven weeks after the 90 percent reduction in the number of bags in unit 5, it was observed that the dust loading in the bags reduced the air flow rate through this unit by 20 percent. Upon analysis, it was observed that the dust mass per bag (after seven weeks) was about twice that in each bag in unit 4.

The total collection rate for all five baghouses was computed to be about 0.5 kilogram of dust per week. It should be noted, however, that the collection rate during the January to June period should have risen to one kilogram per week as judged from the measured collection efficiencies. One cause for this factor-of-two discrepancy may be the loss of mass due to volatilization of the material as it is "dried" by the air flowing through the filter bag.

A small sample of urban dust, subjected to a preliminary analysis by x-ray fluorescence spectrometry shows that the following elements can be observed by instrumental analysis: Ca, Mn, Fe, Co, Cu, Zn, As, Br, and Pb. It would appear, therefore, that this method deserves consideration as a candidate for a relatively inexpensive analytical technique for checking homogeneity of the bulk material at various stages of the SRM production.

On the basis of the observations noted above, it was predicted that the desired quantity of dust would be collected by late winter. Accordingly, the collection operation was discontinued April 6, 1976.

A special vacuum cleaner, provided with a probe of approximately the internal diameter of the bags, was constructed and used at NBS to recover the collected material. The dust so obtained contains a small amount of extraneous material, including bag filters, but this can be removed by sieving. It has been found that more than 90 percent of the recovered material will pass a 325 mesh screen and this appears to be essentially free of bag fiber and sufficiently homogeneous for use as a reference material.

The certification analyses will be conducted during Fiscal Year 1977. It is expected that the SRM will be ready for issue on or about July 1, 1977.

25 SEM and ESCA as Techniques for Characterization of the St. Louis Air Particulate

Project Leader: A. W. Ruff, Metallurgy Division
Other Personnel: D. B. Ballard, A. J. McAlister

Objective

To characterize St. Louis air particulate samples and certain asbestos fibers.

Approach

Scanning electron microscope (SEM) and ESCA examinations have been conducted of the St. Louis, Missouri air sampling station. Asbestos fibers were also studied.

Progress

SEM - A specimen of the proposed SRM Urban Air Particulate, collected at a baghouse station in St. Louis, Missouri, was prepared for examination in the SEM. The technique consisted of sprinkling part of the homogenized sample onto a specimen stub that had previously been covered with a piece of double-stick tape and then coated with a thin layer of carbon. The stub was inverted and tapped lightly to remove excess and nonadherent particles. This prepared specimen was then coated with a 500A layer of Au-Pd alloy by DC sputtering. The specimen was viewed in the SEM with gun potential at 10KV, 23° tilt angle on stub and a target current of 340 x 10^{-12} amp.

The photomicrograph, Figure 25.1 shows particulates typical of the great variety of sizes, shapes and structures observed. Stereomicroscopy was used to ascertain geometrical shapes of some particles. The 3-D technique may allow identification by reference to other SEM publications on particulates and to the McCrone Particle Atlas. The disk shaped particle in Figure 25.2 is probably a pollen grain. Figure 25.3 shows a tentacle-shaped object "A" probably related to a plant seed. The object "B" may be the residue from an incinerated hydrocarbon material. The large particle in Figure 25.4 has fracture surfaces similar to glass. The substructure shown in Figure 25.5 is similar to that seen in a cross section of spruce wood. Many smaller and agglomerated unidentified particles can be seen embedded in or attached to the larger particles described above.

Two materials other than glass were examined in the SEM as substrates for collected air particulates. The first was a paper made from compressed spun-glass fibers and the second was a polycarbonate nuclepore filter paper. Both of these filters were located in the exit stage area of the Delvon Sampler discussed earlier, therefore, the total number of particulates trapped was small. The surface structure of the nuclepore filter is shown in Figure 25.6. Very few particles smaller than the pore size were observed on the surface. A significant number of paired holes can be observed in this filter material. The latter substrate offers the considerable advantage of retaining the particles on one surface rather than permitting them to become embedded within the filter.

Study of Asbestos Materials - A preliminary SEM examination was made on six different bulk samples of asbestos minerals mined at different localities. The specimens were freshly fractured and then mounted on SEM stubs and coated by sputtering with the Au-Pd alloy.

The typical fibrous structure of asbestos is shown in photomicrographs of three of the samples. Figure 25.7 is an amphibole from Bozeman, Montana; Figure 25.8 is a crocidolite from Grigualand, South Africa; and Figure 25.9 is a crysotile from Globe, Arizona. A decrease in fiber flexibility from amphibole to crysotile can be inferred. Also observed were the random occurrence of small irregular particles, probably inclusions of other mineral species, of a nonfibrous nature. Mechanical shredding of this bulk material could radically alter the observed appearance and thus make identification of air collected asbestos particulates by shape and size alone unreliable.

ESCA - Presented here are the results of our effort to evaluate the utility of the ESCA technique for characterization of the St. Louis particulate matter. Withdrawals from our aliquot of the material have been examined in three different ESCA machines.

The major practical problem encountered in these measurements is that of suitably mounting the material which consists of all collected matter which passed a 50 mesh sieve. The particles vary widely in physical characteristics and size[1] are both organic and inorganic in nature [1]. Mounting without cements (using fine screens, heavily etch-pitted metals, and soft metal substrates) was attempted and found wanting, even in the DuPont machine where a favorable horizontal sample mount is used. We therefore followed the practices of the machine operators and employed cemented mounts: double sided scotch tape for the Varian and DuPont machines, and a layer of quick drying silver printed circuit paint for the MacPherson instrument. In all cases, thick, apparently uniform layers of the particulate matter were obtained, and effects of the cement were estimated to be minimal.

In Table 25.1 are summarized the results of ESCA scans of 4 withdrawals studied as mounted, without cleaning. We give here the intensities, relative to the C 1s line intensity, of the strongest observed line of each of the 14 elements identified. The scans (labelled 1, 2, 3, and 4, and identified in the Table 25.1 legend) covered a binding energy range of 0 to 1000 eV; some elements could have gone undetected on account of this limitation. The cited errors of Table 25.1 and later are the estimated counting errors in the data. Results of 3 preliminary runs of the Varian instrument are omitted here because of their high noise level.

In Table 25.2 we present the average of the Table 25.1 data, and convert it to relative atomic concentration in the radiating volume by means of measured relative core level photoexcitation cross-sections[2]. Also shown in Table 25.2 are line intensities obtained from withdrawal No. 1 after 10 minutes of argon bombardment (at a current density sufficient to erode away 15A of SiO_2 per minute, according to the machine operator), and the corresponding atomic concentrations in the radiating volume.

The data for four separate scans on uncleaned, as mounted particulate matter presented in Table 25.1 agree within the noise. Scan 1 took $\simeq$ one hour, and scan 2 eight, on the MacPherson machine; scan 4 12 hours on the Varian instrument; and scan 3, comparable to the 2-hour scan 1 in signal to noise ratio, was obtained in a 20-minute run on the DuPont machine which is designed for fast, low resolution scans. Despite the time investment, only the C and O 1s intensities are established with any real accuracy; the presence of the other lines is established beyond question, but their amplitudes are not accurately established.

The results for the sputter cleaned sample in Table 25.2 should more closely resemble the bulk composition of the material, and it would be of interest to compare them with the results of other analytic procedures.

Chemical speciation [3] is the real power of the ESCA technique. We have made no attempt to identify the chemical species present in the present sample, but the potential for such identification is present and may prove of interest.

References

[1]. See the scanning Electron Microscope studies of this material performed by the Microstructure Characterization Section, 312.03. Amorphous, filamentary, and clearly crystalline structures were observed. Pollen particles were frequently seen and readily identified.

[2]. Jorgensen, C.K. ,and Berthou, H., *Faraday Disc.*, 54,1973.

[3]. Siegbahn, K., Nordling, C., Fahlamn, A., Nordberg ,R., Hamrin, K., Johansson, G., Bergmark, T., Karlsson, S.E., Lindgren, I., and Lindberg, B., *ESCA,Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy.* (Almqvist and Wiksells AB, Stockholm, Sweden, 1967).

Figure 25.1 St. Louis Urban Air Particulate Dust

Figure 25.2 Disk shaped particle is pollen grain

Figure 25.3 Tentacle shaped object "A" related to a plant seed. Object "B" residue from an incinerated hydrocarbon material

Figure 25.4 Large particle has fracture surfaces similar to glass

Figure 25.5 Similar to that seen in a cross section of spruce wood

Figure 25.6 Polycarbonate nuclepore filter located in final stage Delvon sampler 11/29/74

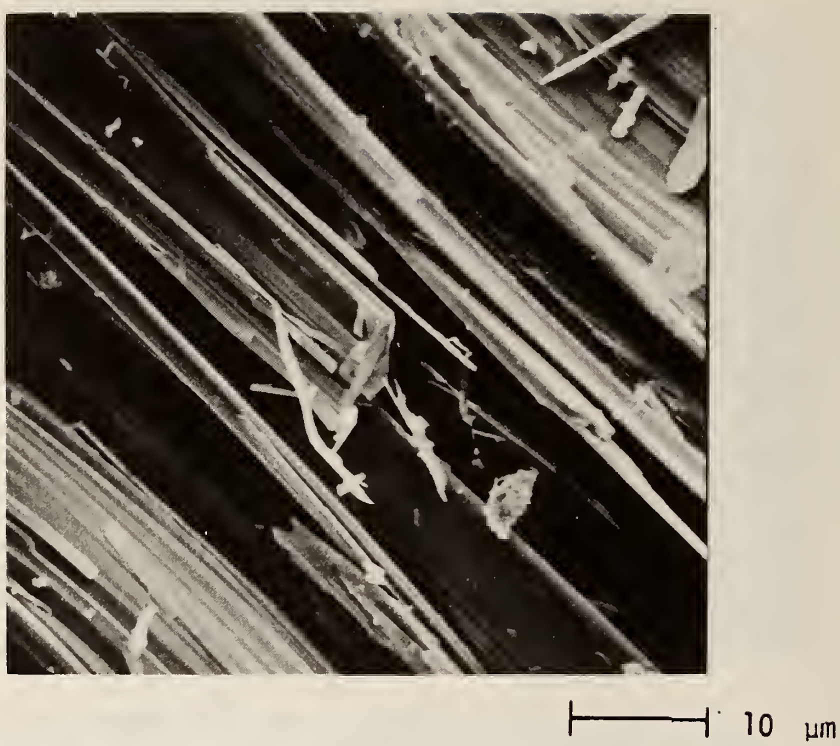


Figure 25.7 An amphibole from Bozeman Montana

Figure 25.8 Crocidolite from Grigualand, South Africa.

Figure 25.9 Crysotile from Globe, Arizona.

Table 25.1 Relative Intensities of Elements in Uncleaned Sample

Element	Level	Withdrawal Numbers 1	2	3	4
C	1s	1.00 ± .08	1.00 ± .02	1.00 ± .07	1.00 ± .01
O	1s	.67 ± .05	.63 ± .02	.70 ± .07	.62 ± .02
Ca	2p	.06	.07	.05	.05
N	1s	.10	.08	.07	.06
S	2p	.03	.03	.01	.01
Si	2p	.04	.03	.03	.03
Mg	2p	.02	.02	--	.02
Al	2p	.01	.01	.01	.01
Cl	2p	.02	.01	--	.03
P	2p	.01	.01	<.005	.01
Na	KLL	.03	.03	--	.02
Pb	4f	.01	.01	<.005	.004
Fe	2p	--	.01	.03	.02
F	1s	--	--	--	.005

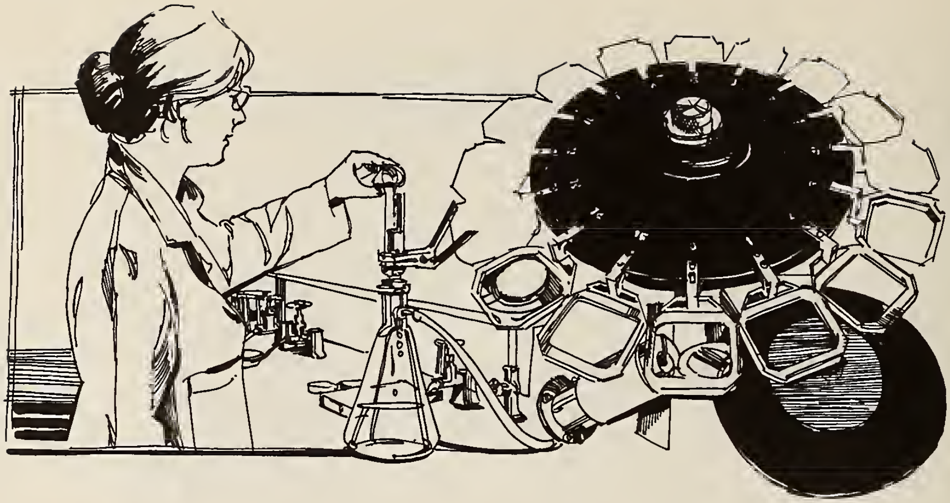
Withdrawal Identifications:

1,2 - MacPherson, Ag paint mount, pressure $\sim 5 \times 10^{-8}$
3 - Dupont, double tape mount, pressure $\sim 5 \times 10^{-6}$
4 - Varian, double tape mount, pressure $\sim 10^{-7}$

Table 25.2. Average of Table 25.1 data and line intensities

Element	Level	Relative Cross Sections	Intensity	Atomic fraction	Intensity	Atomic fraction
C	1s	.27	1.00	.650	1.00	.477
O	1s	.60	.63	.184	1.22	.262
Ca	2p	.80	.06	.013	.23	.037
N	1s	.40	.07	.032	.04	.013
S	2p	.35	.02	.010	.02	.008
Si	2p	.26	.03	.021	.12	.059
Mg	2p	.10	.02	.035	.02	.026
Al	2p	.18	.01	.010	.05	.036
Cl	2p	.42	.02	.009	.02	.006
P	2p	.30	.01	.005	.02	.009
Na	KLL	.39*	.025	.010	.02	.006
Pb	4f	.32	.007	.004	.01	.004
Fe	2p	.18	.015	.014	.07	.050
Fl	1s	1.00	.005	.001	.04	.040

*Inferred from Refs. 2 and 3



26. Development of a Particulate Reference Sample on Membrane Filters for the Standardization of X-Ray Fluorescence Spectrometers

Project Leader: P. A. Pella, Analytical Chemistry Division
Other Personnel: E. C. Kuehner and W. A. Cassatt

Objective

In the analysis of ambient air particulates, the sample analyzed is often in the form of thin deposits on either membrane or Whatman type filters. Therefore, it is desirable to have a calibration sample in the same form. The preparation of orchard leaf deposits on membrane filters to be used for this purpose is described in this report. The work was supported by the Environmental Protection Agency.

Approach

The NBS Orchard Leaves (SRM 1571) as certified requires that at least 250 mg samples be taken to insure that the trace element distribution is representative of the bulk material. To permit smaller samples to be used and to minimize the attenuation of x-rays in the individual particles, the material was reground. A number of different coatings were investigated to provide good sample protection, and at the same time obtain low attenuation of the x-rays from elements such as phosphorus and sulfur. Different coating materials that were investigated consisted of polyisobutylene, heat-sealed overlays of polypropylene and Parafilm, and vapor-deposited Parylene films.

Progress

Sample deposits were prepared by filtration of a suspension of the reground material in cyclohexane. Attempts were made to prepare deposits from an aerosol suspension, but were not successful.

A. Grinding of the Orchard Leaves SRM 1571

A high velocity air impact grinder was used to reduce the particle sizes. The impactor produces two size fractions having relatively broad size distributions. The "fines" fraction was collected after each pass through the grinder and was reground four times. The particle size distribution of the collected material was characterized by automated image analysis. Data were taken by examining nine regions of four different sample preparations. These samples were prepared by dispersing a few milligrams of material in cyclohexane with ultrasonic stirring. About three drops of this suspension were placed on a microscope slide, covered with a cover glass and allowed to dry.

B. Preparation of Deposits on Membrane Filters

From 2 to 15 mg of dried reground orchard leaves were weighed and transferred to a 50 ml beaker containing about 40 ml of spectrograde cyclohexane. The beaker containing the orchard leaves was placed in an ultrasonic bath for about one minute to disperse the particles. The suspension was transferred to a vacuum filtering unit and the sides of the beaker were washed down with cyclohexane. The material was filtered rapidly through a 37 mm preweighed membrane filter (0.8 μm pore size). The glass filtering funnel was constructed so that deposits on the 37 mm membrane filters were 29 mm in diameter. The net weight of the air-dried deposit was used to calculate the areal density of the deposit in mg/cm^2. All weighings were performed in a room in which the relative humidity was maintained at 50 ± 4 percent.

C. Preparation of Parylene-Coated Samples

The samples were coated at the Union Carbide Corporation with a thin film of Parylene N--a polymeric material developed by Union Carbide Corporation (U. S. Patent No. 3342754). The procedure consists of first vaporizing the di-para-xylylene dimer by heating it at 175°C at 760 mm Hg ($1.01 \times 10^5 N/m^2$). This vaporized material passes through a deposition chamber maintained at room temperature, and 0.1 mm Hg ($13.3\ N/m^2$) which contains the samples to be coated. The samples are rotated in the chamber to insure a uniform coating of Parylene. The exit of the deposition chamber is connected to a cold trap (-70°C) and pumped with a mechanical pump to a pressure of 0.001 mm Hg ($0.133\ N/m^2$). The film thickness is monitored in the deposition chamber using a piezoelectric frequency sensor. More accurate thickness measurements were made at Union Carbide after removal of the samples using a UV spectrometer. The thickness is calculated from a calibration curve by comparing the absorbance of the film with that of a film of known thickness measured interferometrically.

D. Preparation of Thin-Film Overlays of Parafilm and Polypropylene

A sheet of Parafilm (American Can Co.) was stretched by hand as thinly as possible without causing the sheet to tear, and was placed directly on the sample which was held by suction to a filtering funnel. A polypropylene sheet (0.08 mm thick) was next placed on top of the Parafilm and was heat-sealed to the sample using a hot air gun.

E. Mounting the Parylene-Coated Filter Deposit

Filter holders for mounting the deposits were supplied by EPA, and are described in an EPA report[1] These holders, designed to accommodate 37 mm diameter membrane filters, were modified by increasing the platform diameter by 2 mm. This permitted the filter deposit to be centered in the holder more easily and also allowed for some expansion of the membrane filter before cementing in the holder. The filter deposit was held on a filtering funnel by applying suction. A thinned mixture of cement prepared by mixing equal parts of Barge all-purpose cement, ethyl acetate and cyclohexane was brushed on the platform of the holder. The filter was cemented to the holder platform by pressing the holder flat against the outer edge of the filter deposit and then allowed to dry.

Neutron activation analysis (NAA) of the reground orchard leaves showed that the concentrations of iron, nickel, cobalt and chromium were much higher than in the certified SRM 1571. Therefore, it was important to determine if these introduced elements were homogeneously distributed throughout the material. For this reason, sixteen samples of reground material (200 mg each) were taken and six elements, including iron and chromium, were analyzed by NAA. An analysis of variance of these concentrations in the material indicated that there were no gross inhomogeneities (not greater than five percent). These results indicated that the reground SRM 1571 was satisfactory for use provided that recertification of the introduced elements could be accomplished.

The particle size distribution of the reground material is shown in Figure 26.1. The area of about 80 percent of the 3000 particles examined was between zero and 7.5 μm^2 (3.1 μm equivalent diameter). Less than 0.5 percent of the particles were within 82.5 and 105 μm^2, with no particles observed above 105 μm^2.

To determine if the cyclohexane treatment altered the trace element composition of the orchard leaves, NAA was performed on cyclohexane extracts and on the material after treating with cyclohexane. A number of elements, including Br, Mn, Fe, K, and Na were analyzed. The results showed that only sodium was affected by this treatment, and about 50 percent was extracted.

A simple technique was developed for measuring the uniformity of the deposits. This consisted of directing a laser beam about 2 mm in diameter normal to the sample, and measuring the intensity of the light transmitted [2]. Using A Beer's law calibration of absorbance vs. areal density, the uniformity of the deposit was measured. Of the several samples examined having areal densities of 1.0 to 2.0 mg/cm^2, variations in uniformity did not exceed 0.02 mg/cm^2.

A number of coating materials were investigated and compared with regard to their ability to adhere to the sample and to provide protection from abrasion and humidity. These consisted of vapor-deposited Parylene films and heat-sealed overlays of polypropylene using Parafilm as a binder. Also, orchard leaf deposits were prepared from suspensions in cyclohexane containing from 0.1 to 10 percent by weight of polyisobutylene. Another important factor considered was the x-ray attenuation of these coatings, especially from elements of low atomic number such as phosphorus and sulfur. The attenuation of P, S, K, and CaKα lines was measured by comparing the background corrected peak intensities of coated and uncoated samples having the same areal densities using a wavelength-dispersive x-ray spectrometer.

The values obtained for various thicknesses of Parylene and of thin polypropylene and Parafilm coatings are summarized in Tables 26.1 and 26.2, respectively. For Parylene coatings 75 to 193 nm thick, little change in attenuation was noted. Also, the x-ray background intensities from these samples were essentially the same as the uncoated samples except that the background of the 2500 nm thick sample was increased significantly. The attenuation values of the polypropylene-Parafilm coatings could not be reduced any further because thinner films were not available. In order to produce adherent deposits using polyisobutylene, as much as one percent or greater by weight of the polymer in cyclohexane was used. However, the amount of polyisobutylene retained on the samples varied considerably making it difficult to obtain reproducible attenuation data. For this reason, this coating material was considered unsatisfactory.

Table 26.1. Average Attenuation Values of Parylene Coatings[a]

sample areal density = 2.0 mg/cm^2

No. of Samples	Parylene Thickness, nm	Element	Percent Attenuation	
			Average	S[b]
5	75	P	3	1.7
3	75	S	2	1.3
2	75	K	1.4	---
5	117.5	P	3.1	0.50
5	117.5	K	1.7	0.44
5	158.0	P	5.4	0.90
2	158.0	S	5.2	---
4	158.0	K	2.9	0.35
7	166.5	P	5.0	0.81
5	166.5	S	4.3	0.92
7	166.5	K	2.6	0.69
5	193.0	P	7.3	0.88
3	193.0	K	3.7	0.20
3	2500	P	33	1.5
3	2500	S	28.9	0.71
2	2500	K	11.4	---

[a] Calculated from the expression $I_u - I_c / I_u$ x 100; where I_u = peak intensity of uncoated sample, and I_c = peak intensity of coated sample.

[b] S = standard deviation of a single measurement.

Table 262 Attenuation Values of Polypropylene and Parafilm Coatings

Sample #	Total Coating Thickness, mg/cm^2	Percent Attenuation P	S	Cl	K	Ca
1	1.2	28.1	23.2	14.1	10.9	8.5
2	1.1	24.4	23.6	16.2	11.4	7.9
3	1.2	26.3	24.4	13.6	10.1	8.3
Average		26.3	23.7	14.6	10.8	8.2

The ruggedness of samples coated with Parylene films (75 to 200 nm thick) were tested by an air jet which impinged on the sample surface. Effects of humidity were observed when the samples were placed in a chamber maintained at 100 percent relative humidity.

The trace element composition of the starting material (di-para-xylylene dimer) was analyzed at Union Carbide Corporation. Of the 27 elements analyzed, sodium, magnesium, iron and aluminum were present in concentrations from 2 to 9 ppm. Silicon was 31 ppm, and the remaining elements were either below 1 ppm or were not detected. These results indicate that the Parylene material should be of sufficient purity for application in this work. Since the Parylene films appeared to furnish good sample protection, including high resistance to humidity, high purity, good adherence, and acceptable x-ray attenuation for the low atomic number elements, 60 samples were prepared and delivered to EPA containing from 0.1 to 5.0 mg/cm^2 of orchard leaves coated with 117.5 nm of Parylene.

References

[1]. Goulding, F.S., and Jaklevic, J.M., *EPA Report No. EPA-R2-73-182*, April 1973.
[2]. Kuehner, E.C., and Cassatt, W.A., *A Laser Microphotometer for Determining Uniformity of Particulate Deposits on Membrane Filters*, in press.

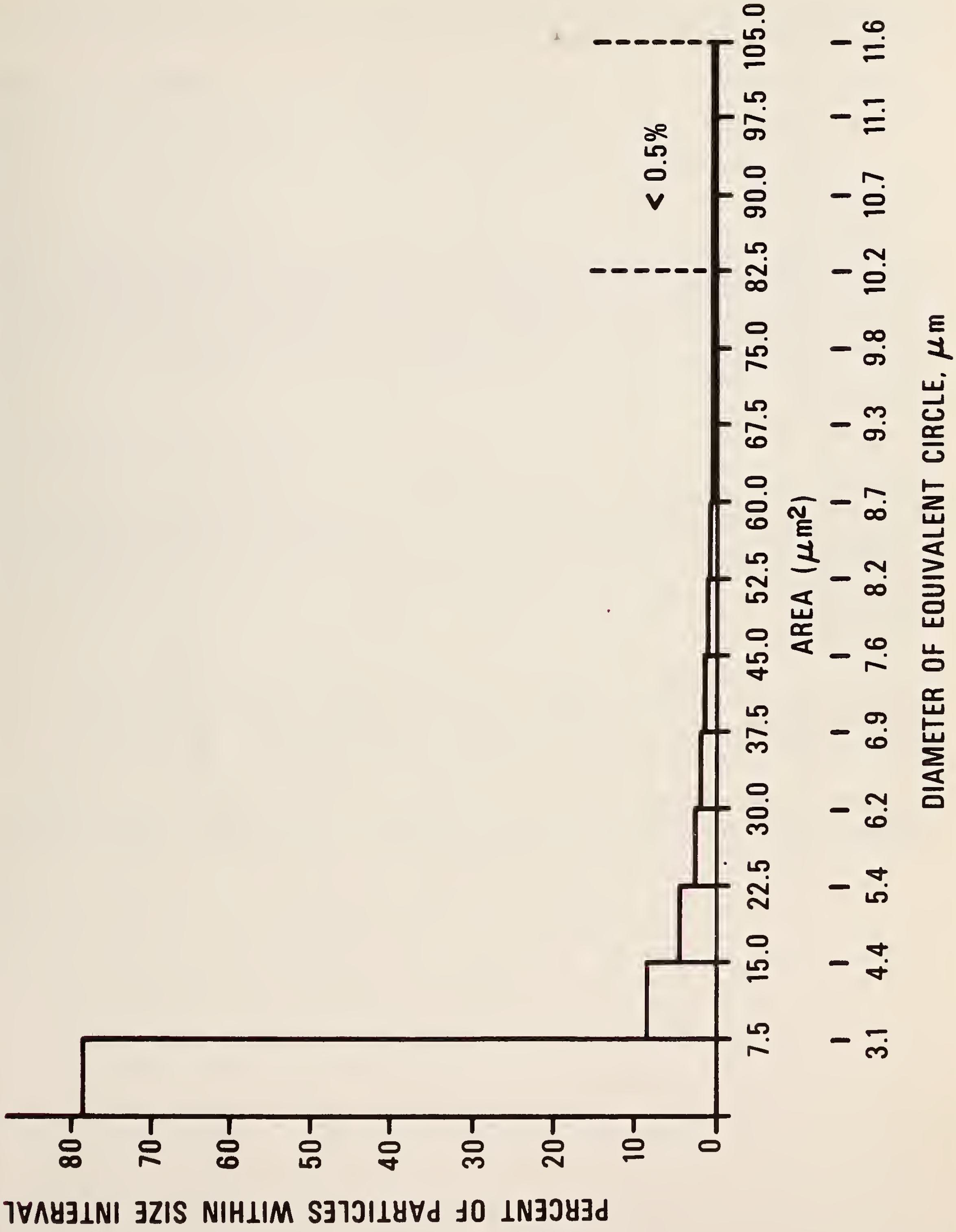


Figure 26.1 Particle size distribution of reground material

27. Analysis of EPA X-Ray Calibration Standards by Isotope Dilution Mass Spectrometry

Project Leader: I. L. Barnes, Analytical Chemistry Division

Other Personnel: L. J. Moore, L. A. Machlan, J. W. Gramlich

Objective

As part of a study by the x-ray analysis laboratory (ERC) at the Environmental Protection Agency to develop accurate calibration standards for their energy dispersive x-ray fluorescence spectrometer, a set of vacuum deposited mylar foils was analyzed destructively by isotope dilution thermal ionization mass spectrometry (IDMS) at NBS.

A set of foils, with each foil containing a single deposit of CuS, KCl, CaF_2, Cr, Fe, Cu, $RbNO_3$, SrF_2, MoO_3, or Pb was analyzed for cation content by IDMS. The deposits were also carefully characterized by EPA for uniformity using proton-induced x-ray emission analysis. The results of these calibrations indicate that disagreements as large as 15 percent were observed between standards from the two commercial suppliers.

Follow-up analyses for Ca, Ba, Sr, and Pb by IDMS for a second set of filters have not yet been evaluated in an effort to elucidate problems in the characterization of these deposits for use as EDXRF calibration standards.

Summaries of the IDMS work at NBS and the goals of the EPA project are presented in the attached report and publication.

July 14, 1976

Report of Analysis

A set of x-ray calibration foils (Set #2) was analyzed by thermal ionization isotope dilution mass spectrometry for Ba, Ca, Sr, and Pb. Four foils, each containing a single element in the form of a salt or metallic deposit, were each carefully removed from the supporting frames and spiked with the appropriate separated isotope (^{84}Sr, ^{42}Ca, ^{135}Ba, ^{206}Pb). After acid dissolution and isotopic equilibration, each sample was purified by ion exchange and analyzed isotopically by well established mass spectrometric procedures.

A set of foils previously analyzed (1975) in a similar fashion and reported in a publication [1] are also listed in table 27.1 for convenient reference.

The errors indicated are estimated overall limits of error for a single analysis, which are based on a large number of similar analyses previously performed for a particular element.

[1] Stiles,A.R.,et al.,Calibration of an EDXRF Spectrometer, *Advances in X-ray Analysis*, 19, (1975).

Table 27.1
X-RAY CALIBRATION FOILS

	Total analyte, µmols		
	Set #1	Set #2	Estimated Limit of Error for a Single Analysis, Relative
Ba	1.154	1.067	0.20%
Ca	1.817	1.585	0.10%
Sr	1.219	1.239	0.10%
Pb	1.142	1.007	0.10%
Mo	1.395	---	0.20%
K	2.833	---	0.15%
Cu	3.326	---	0.25%
Fe	1.350	---	0.70%
Cr	1.666	---	0.25%
Rb	1.512	---	0.15%

CALIBRATION OF AN ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETER

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Abstract

The purpose of this work was to develop accurate calibration standards which were fully characterized in terms of uniformity and concentration using fundamental measuring methods. Three similar sets of vacuum deposits were commercially made, each set containing the single deposits CuS, KCl, CaF_2, Cr, Fe, Cu, $RbNO_3$, SrF_2, MoO_3, BaF_2, and Pb. Thickness variations in each deposit were measured with PIXEA (proton induced x-ray excitation analysis) measurements taken at 6 to 8 positions along the deposit diameters. Relative elemental concentrations on corresponding deposits from each set were measured using multiple XRF intercomparisons. One set of deposits was destructively analyzed at the National Bureau of Standards with isotope dilution thermal ionization mass spectrometry (IDMS) in order to calibrate the remaining sets of vacuum deposits. The calibrated deposits were compared with standards from two commercial sources. For seven elements heavier than chlorine there was an average deviation of 13.5% between the calibrated deposits and the commercial standards. Disagreements as large as 15% were observed between standards from the two commercial suppliers.

Introduction

Calibration standards for thin sample analysis are available commercially as solution deposits on membrane filters and as vacuum deposits on thin Mylar. Significant disagreements between standards from different commercial sources have been observed in our laboratory using an energy dispersive x-ray fluorescence (EDXRF) spectrometer. Alternatives to the use of commercial standards are the preparation of laboratory calibration standards, using solution deposition, pressed pellets, vacuum deposition or other techniques. The approach adopted in this work was the accurate characterization of vacuum deposits on thin Mylar for 12 elements and preparation of solution deposited two-element ratio standards for the other elements of interest. The calibration program consisted of the following steps: 1. Characterization of the EDXRF spectrometer. 2. Characterization of three similar sets, A, B and C, of vacuum deposits for 12 elements using PIXEA to measure uniformity and XRF spectrometry to establish interset ratios for each element. 3. Destructive analysis at the NBS of set A of vacuum deposits using IDMS (isotope dilution thermal ionization mass spectrometry). 4. Calculation of true concentrations and soft x-ray attenuation corrections for foil sets B and C based on the IDMS results. 5. Preparation of two-element solution deposited ratio standards to link the 12 calibrated elements with other elements of interest.

System Parameters

The EDXRF spectrometer calibrated in this study uses a 30 watt tungsten anode x-ray source to excite three secondary targets, Ti, Mo and Sm [1,2]. The Si(Li) detector has a guard- ring reject feature [3] to reduce errors due to partial charge collection. Spectral analysis is accomplished with a minicomputer using stored shape standards. The system is dedicated to the analysis of atmospheric aerosols collected on membrane filters. A diagram of the sample chamber is shown in Figure 27.1.Standards and samples analyzed in this system are mounted in plastic frames Figure 27.2a which can accommodate 37 mm diameter specimens. Figures 27.2b and 27.2c are the result of measurements to determine the sensitivity of the spectrometer to sample displacements and non-uniformities. The sample plane, x-y, was mapped by positioning Pb-Sn solder squares on graph paper substrates using a thin layer of grease for adhesion. The importance of uniform thickness for standards and samples is evident with this highly non-uniform beam configuration. The effect of displacements along the z-axis due to warped or out-of-plane samples was investigated using shims with both solder squares and solution deposits on filter paper.

Most imprecision, exclusive of counting statistics, can be ascribed to variations in the output of the x-ray tube. With ± 0.5% line voltage regulation, the count rate of this spectrometer can vary within ± 1-5%, depending upon the secondary target and anode voltage. An additional ± 2% (2σ) uncertainty, inferred from the residual errors in the XRF ratio measurements described in the next section, is attributed to instability

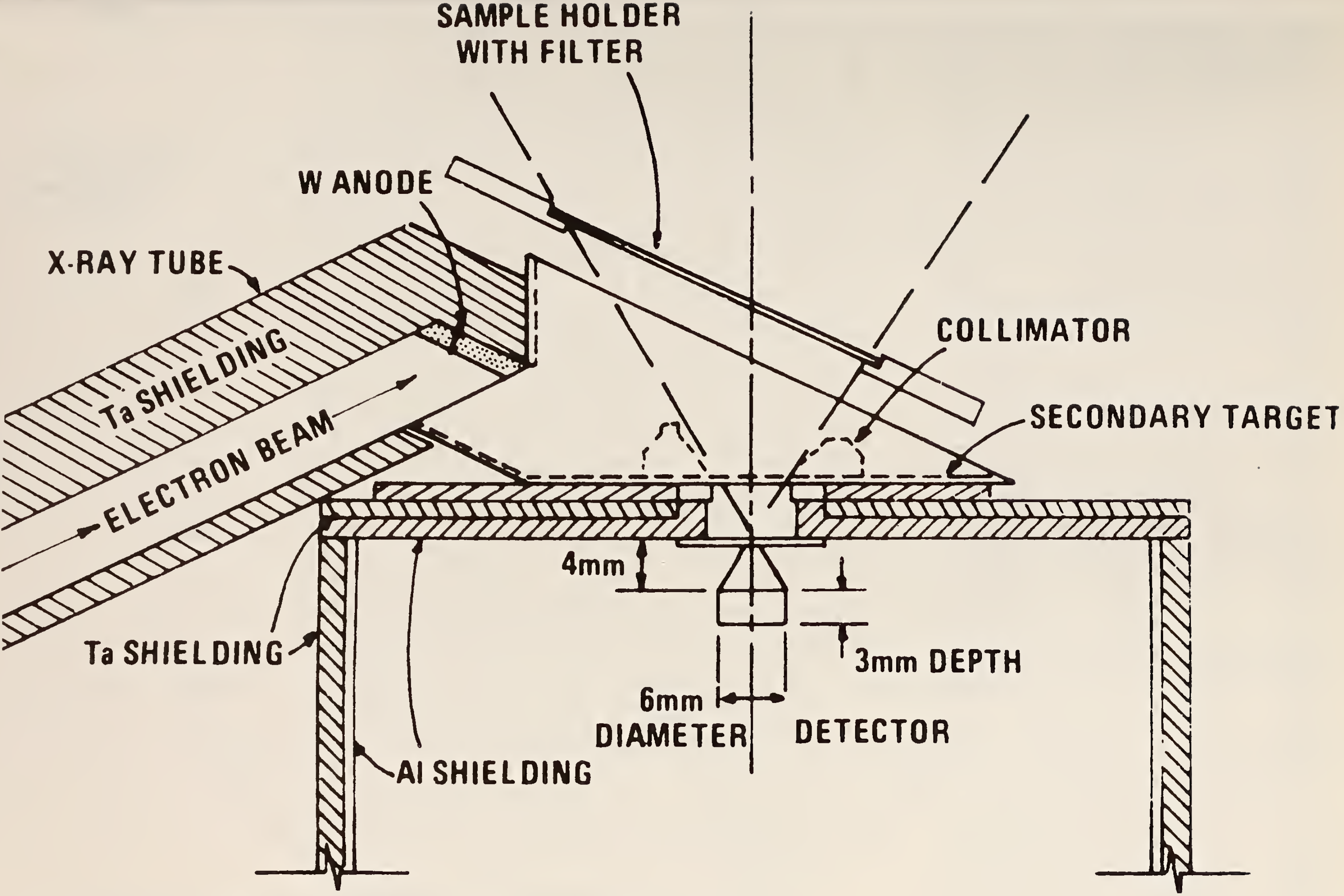
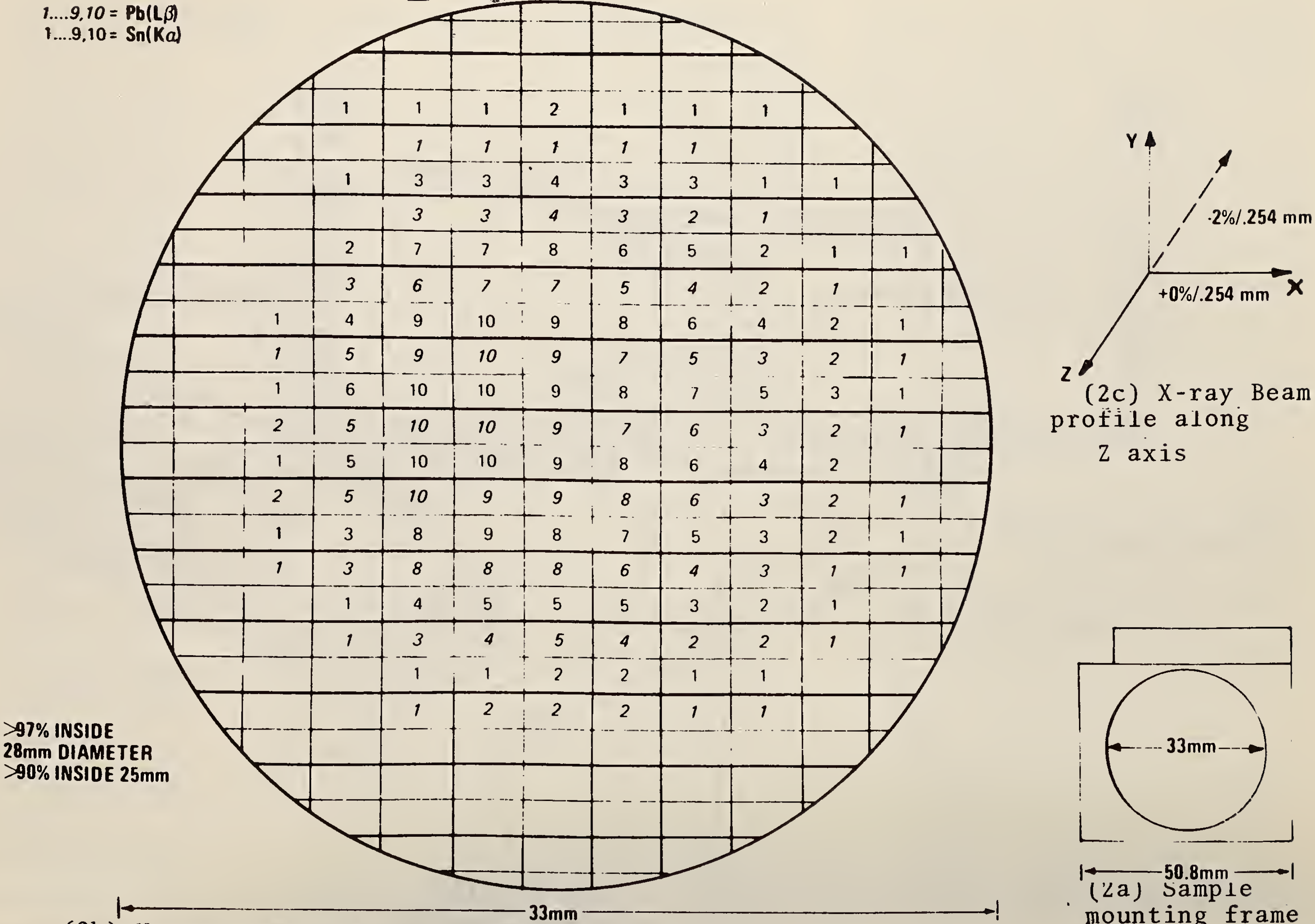


Figure 27.1 Sample chamber of EDXRF Spectrometer

Figure 27.2



	1	1	1	2	1	1	1		
		1	*1*	*1*	*1*	*1*			
	1	3	3	4	3	3	1	1	
		3	*3*	*4*	*3*	*2*	*1*		
	2	7	7	8	6	5	2	1	1
	3	*6*	*7*	*7*	*5*	*4*	*2*	*1*	
1	4	9	10	9	8	6	4	2	1
1	*5*	*9*	*10*	*9*	*7*	*5*	*3*	*2*	*1*
1	6	10	10	9	8	7	5	3	1
2	*5*	*10*	*10*	*9*	*7*	*6*	*3*	*2*	*1*
1	5	10	10	9	8	6	4	2	
2	*5*	*10*	*9*	*9*	*8*	*6*	*3*	*2*	*1*
1	3	8	9	8	7	5	3	2	1
1	*3*	*8*	*8*	*8*	*6*	*4*	*3*	*1*	*1*
	1	4	5	5	5	3	2	1	
	1	*3*	*4*	*5*	*4*	*2*	*2*	*1*	
		1	1	2	2	1	1		
		1	*2*	*2*	*2*	*1*	*1*		

(2c) X-ray Beam profile along Z axis

(2a) Sample mounting frame

(2b) X-ray beam profile in sample (x-y) plane within the high voltage supply; it is regarded as a short term error, since its effects were observed in successive measurements of the same sample.

The effect of gain and baseline drifts in the pulse amplifier and ADC was calculated assuming a Gaussian peak shape and a fit region equal to one FWHM (full width at half maximum). A small peak shift in either direction causes an apparent increase in elemental concentration when the spectrum is analyzed with stored shape standards. Peak centroid shifts in excess of 0.1 FWHM are rare, and the corresponding error range is +2 -0%. In routine sample analysis these errors can be minimized with periodic adjustment of pulse electronics and can be virtually eliminated with software that includes mathematical spectrum shifting or functional peak representations.

Characterization of Vacuum Deposited Films

Essential properties for the elemental deposits characterized in this study were 1) ability to withstand the beam-heating of PIXEA with a 3 MeV proton beam of 5-20 nA, 2) uniformity of the deposit thickness, 3) high XRF peak/background, 4) known area of deposit, 5) amenability to accurate attenuation correction, and 6) flatness. Properties 1, 3, 4 and 5 argued effectively for vacuum deposits on thin (4 μm) Mylar. Accordingly, three similar sets of vacuum deposits on Mylar were obtained, each set A, B and C consisting of the separate deposits CuS, KCl, CaF_2, Cr, Fe, Cu, $RbNO_3$, SrF_2, MoO_3, BaF_2 and Pb. A well defined area of 7.92 cm^2 was obtained using a circular, 31.75 mm diameter knife-edge aperture to mask the Mylar during deposition. The deposits were centered and mounted by the manufacturer (MicroMatter Co., Seattle, WA) in the sample frames provided. The vacuum deposits calibrated in this work were prepared by vacuum deposition at a distance of 20 cm from the evaporator in order to obtain a uniformity of ± 2% or better. The deposits were not weighed by the manufacturer because the range of concentrations, 10-20 $\mu g/cm^2$, was too low for a ± 5% determination.

The uniformity of each vacuum deposit was measured using PIXEA (6 mm dia.) spot measurements at 6 to 8 positions along the deposit diameters. To minimize damage to the target films, the scans were preceded by evaporation tests with zinc and other volatile deposits; it was found that 3.0 MeV proton currents between 10 and 20 nA were safe for all deposits for periods of several minutes. Duplicate measurements were made at each location on the films, each measurement an accumulation of more than 10k counts, to obtain better than 1% statistical precision. For all elements except S, K and Ba the peak-to-background ratios were greater than 100, and it was possible to make relative thickness determinations using a single channel analyzer and scaler to select and count the characteristic x-rays. For the three exceptional elements, an on-line computer code permitting background subtractions and peak area calculations was used in conjunction with a CRT display to measure x-ray yields. Figure 27.3 shows the PIXEA results for an iron deposit. While a standard deviation of thickness for this deposit was found to be 1.8%, the center of the deposit where the EDXRF system is most sensitive was not far, only 0.27%, from the average deposit thickness. This was true for most deposits, as indicated in Figure27.4 a summary of the PIXEA results. Thus, non-uniformity was estimated to have less than ± 2% effect upon the accuracy of these deposits as calibration standards.

Intraelemental ratios, A/B, C/B and A/C, among the three sets A, B and C of vacuum deposits were measured using ten XRF measurements of each deposit. For each element, the anode current was adjusted in order to obtain no more than 2000 counts per second with the thickest deposit. The analysis time for each element was selected to yield more than 10K counts in the principal characteristic peaks and ranged between 30 and 150 seconds, depending upon the excitation efficiency and peak-to-background ratio. Peak-to-background ratios ranged from only 2 for Ba to more than 100 for Pb. Background subtraction was accomplished using a stored Mylar blank spectrum and normalization to a background fit region located above the characteristic peaks. Elemental ratios among sets A, B and C were calculated using the integrated peak counts over a region containing the characteristic peak that was estimated to be large enough to minimize errors due to centroid shifts while not seriously degrading the peak-to-background ratio. The intraelemental ratios ranged between 0.4 and 1.6 with calculated uncertainties averaging about 1% at the 95% confidence level. The error calculations indicated that the XRF ratioing measurements contributed less than ± 1.5% uncertainty to the eventual calibration of these deposits following the NBS analyses. The residual imprecision, after exclusion of counting statistics, was attributed to short-term instabilities in the high-voltage anode supply.

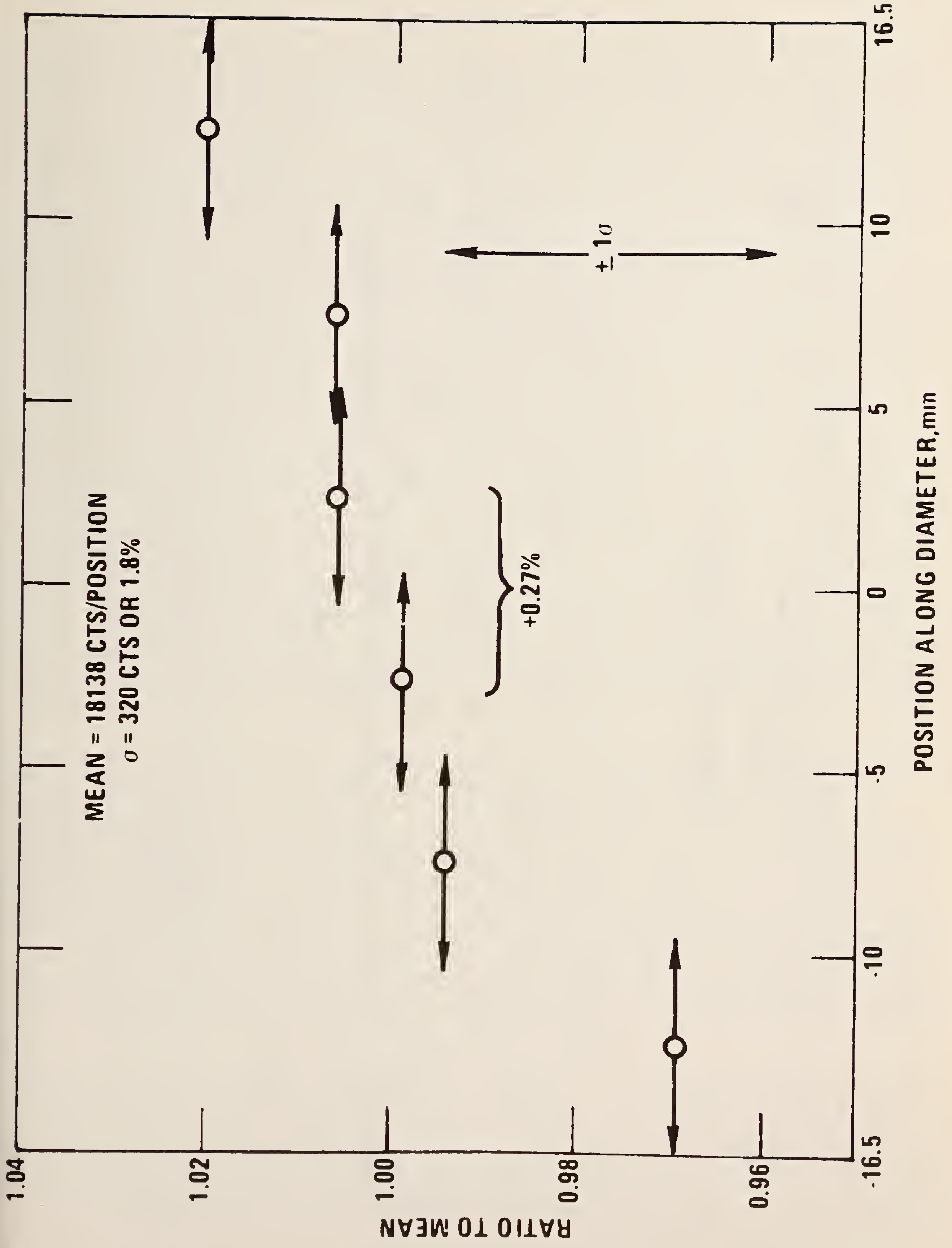


Figure 27.3 PIXEA uniformity measurement of Typical Iron Dust

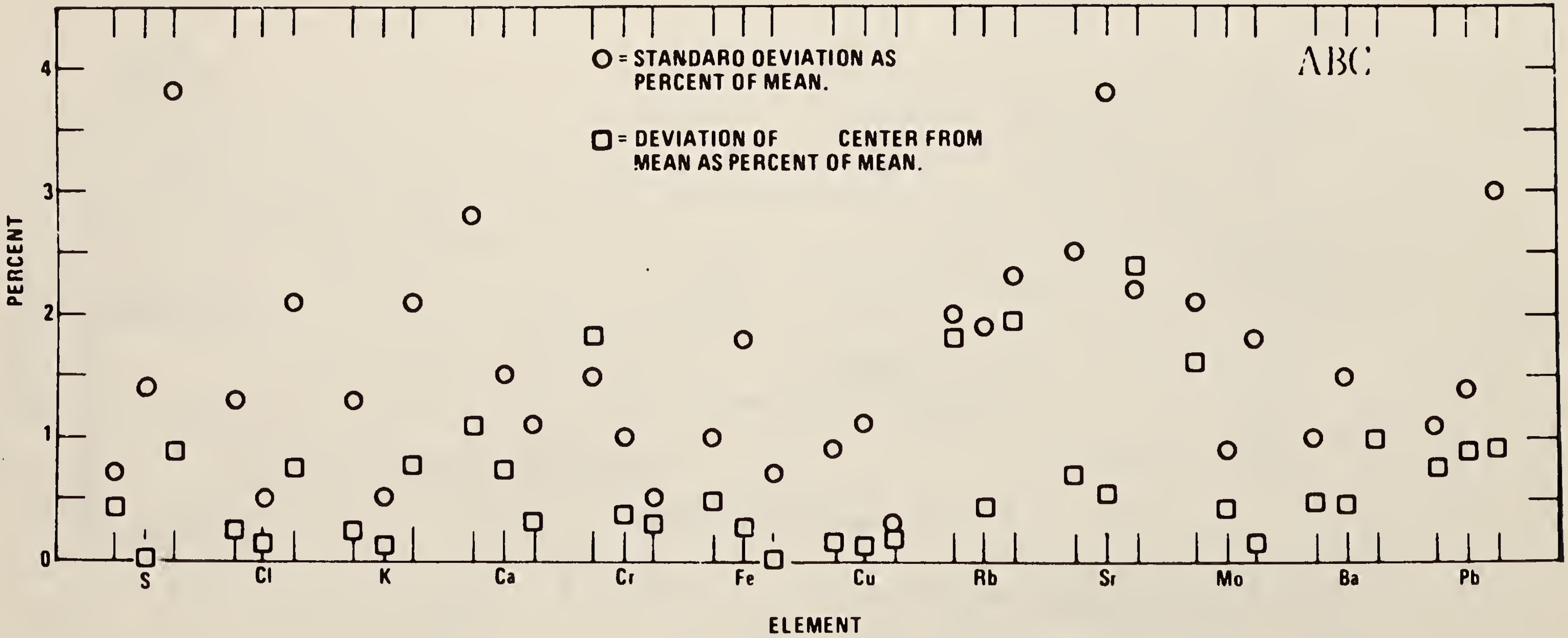


Figure 27.4 PIXEA uniformity Results for deposits A,B, and C for 12 elements

IDMS ANALYSES

Modern isotope dilution trace determinations by thermal ionization mass spectrometry, in conjunction with chemical matrix purification techniques, have resulted in optimal precisions and accuracies ($\lesssim$ 0.1%) that have been equaled by no other analytical technique. The efficacy of IDMS, when rigorously and properly applied, accrues primarily from four sources: 1) The use of an internal standard (the separated isotope) which is atoms of the analyte itself. The accuracy of IDMS is therefore not measurably affected by non-quantitative recovery, as long as a reasonable percentage of the original sample is recovered. 2) The purification of the analyte by ion exchange and other separation techniques, so that a pure sample is derived for isotopic analysis. 3) The present capacity to measure, very precisely and accurately and with a minimum of spectral interferences, stable isotopic ratios of small samples via thermal ionization mass spectrometry. 4) The use of well characterized isotopic and stoichiometric standards and related materials. These four components result in the control or elimination of interferences which often occur with techniques that rely on the observation of some secondary property of the analyte and not the atoms themselves. The demonstrable accuracy of IDMS uniquely qualifies it as a tool for the evaluation of other analytical methods that are less fully developed. IDMS is currently being applied at NBS in such a role to develop reference methods of clinical analysis for the determination of electrolytes in blood serum by atomic absorption/emission techniques.

The pre-characterized vacuum deposited films were carefully removed from their mounting frames while held over a beaker. To each beaker containing a sample was added an accurately weighed (± 0.01%) isotopic spike solution of the corresponding element that had been highly enriched in one of its stable isotopes (^{100}Mo, ^{84}Sr, ^{42}Ca, ^{206}Pb, ^{87}Rb, ^{57}Fe, ^{41}K, ^{65}Cu, or ^{50}Cr). The concentration of each spike solution was calibrated to within 0.1 - 0.2% by comparing it to a natural solution of the particular element which was gravimetrically prepared from well characterized isotopic and stoichiometric standards. After acid dissolution and isotopic equilibration, each spiked sample was purified by ion exchange or extraction.

Isotopic measurements were made using well established procedures [4,5,6] on NBS designed and built single focusing magnetic sector mass spectrometers, capable of providing stable isotopic ratio measurements to less than ± 0.05% [7]. The fractionation error induced by thermal ionization was corrected either empirically by analyzing samples in a manner identical to that of a standard of known isotopic composition or, for elements of three or more isotopes and adequate signal intensity, by internal normalization to a constant natural isotopic ratio.

A separate Pb deposit was isotopically analyzed in order to minimize the effect of radiogenic isotopic components on IDMS accuracy. For Sr, a similar in situ correction was made for the radiogenic ^{87}Sr.

The measured chemical contamination from the chemical processing was very small. Except for Fe, the analytical uncertainty for all elements was less than or equal to 0.25% (relative tσ) [5] the Fe uncertainty was less than 0.7% due to a higher contamination level.

Calibration of Deposits

The two remaining sets of vacuum deposits B and C were calibrated using the IDMS results for set A, the XRF ratios, and the known deposit area of 7.92 cm^2. The element chlorine was calibrated by assuming stoichiometry for the KCl deposits ± 2%. S and Ba were not analyzed with IDMS and will be calibrated using an accurate alternative method at the NBS. Attenuation corrections for representative concentrations of S, K and Ca using Ti excitation are shown in Table 27.2. These values were calculated with the expression [3].

$$A = (1-\exp(-(\mu_1 \sec\theta_i + \mu_o \sec\theta_o)\rho d))/(\mu_i \sec\theta_i + \mu_o \sec\theta_o)\rho d,$$

where μ_i and μ_o are the total mass absorption coefficients (cm^2/g) for the incident and observed radiation respectively, θ_i and θ_o are the angles of incident and observed radiation with the normal to the sample plane respectively and ρd is the concentration of the deposit (g/cm^2). Two cases were considered for each attenuation correction. The CuS deposit was prepared by sulfiding a copper vacuum deposit with sulfur vapor; precipitation of the sulfur onto the copper might also have occured, but the sulfur attenuation correction was estimated by assuming that the formation of copper sulfide was more likely. All deposits with soft characteristic x-rays were examined under a microscope, and the KCl deposits were found to be granular with particle thicknesses estimated to be 2.5 times the average deposit thicknesses; the attenuation correction for potassium was estimated to be somewhat closer to the value obtained for the granular case. Since none of the x-ray attenuations exceeded 4%, the estimated uncertainty in these is no more than 1%.

Table 27.2

ATTENUATION CORRECTIONS

Case	$\mu g/cm^2$[a]	A(Calculated)	A(Estimated)
S(Kα), Sulfide Precipitate	10.0	0.974 0.996	0.98
K(Kα), Layer Granular(2.5)	10.5	0.985 0.963	0.97
Ca(Kα), Layer Granular(2.5)	13.6	0.993 0.982	0.99

[a] Concentrations of S, K and Ca in CuS, KCl and CaF_2, respectively.

Solution Deposited Ratio Standards

Solution deposited ratio standards were prepared in order to link the twelve elements calibrated via NBS analyses with other elements of interest heavier than chromium. The solutions, each containing two elements, one of which was a calibrated element, were deposited onto filter paper with a depositor consisting of a precision capillary matrix. Freeze drying was employed to minimize chromatographic effects. Principle advantages of this technique are repeatability and overall uniformity, both near 3% [8,9]. A disadvantage is that the capillary deposits, like all solution deposits, are not easily corrected for soft x-ray attenuation. A more complete description of this new technique for solution deposition is given in the literature [8,9].

Results and Discussion

Elemental concentrations in routine XRF analyses of samples are calculated using the expression,

$$C_Z(\mathrm{ng/cm^2}) = I_Z N/F_Z,$$

where C_Z is the concentration of element Z, I_Z is the total number of counts contained in the principal characteristic peak for element Z after background subtraction, N is a normalization constant near unity, and F_Z is a calibration constant or F-number for the element Z. Figure 27.5 shows F-numbers that were obtained previously using commercial calibration standards. Because of the unexpected outcome of XRF intercomparisons between the IDMS calibrated deposits and commercial standards discussed in later paragraphs, new F-numbers have not yet been obtained. F-numbers for the twelve elements studied here will be obtained experimentally, while those for intermediate elements will be calculated using XRF data from the solution deposited ratio standards and a weighted nonlinear least squares fit to a smooth calibration curve [3]. Elements lighter than sulfur will be calibrated with vacuum deposited standards instead of solution standards.

Table 27.3 lists the uncertainties associated with data acquisition with samples using the calibrated XRF spectrometer. Entries 1 through 5 in table 27.3 have been discussed earlier. The last entry includes, for the twelve elements calibrated with NBS analyses, the combined uncertainties (rounded upward).

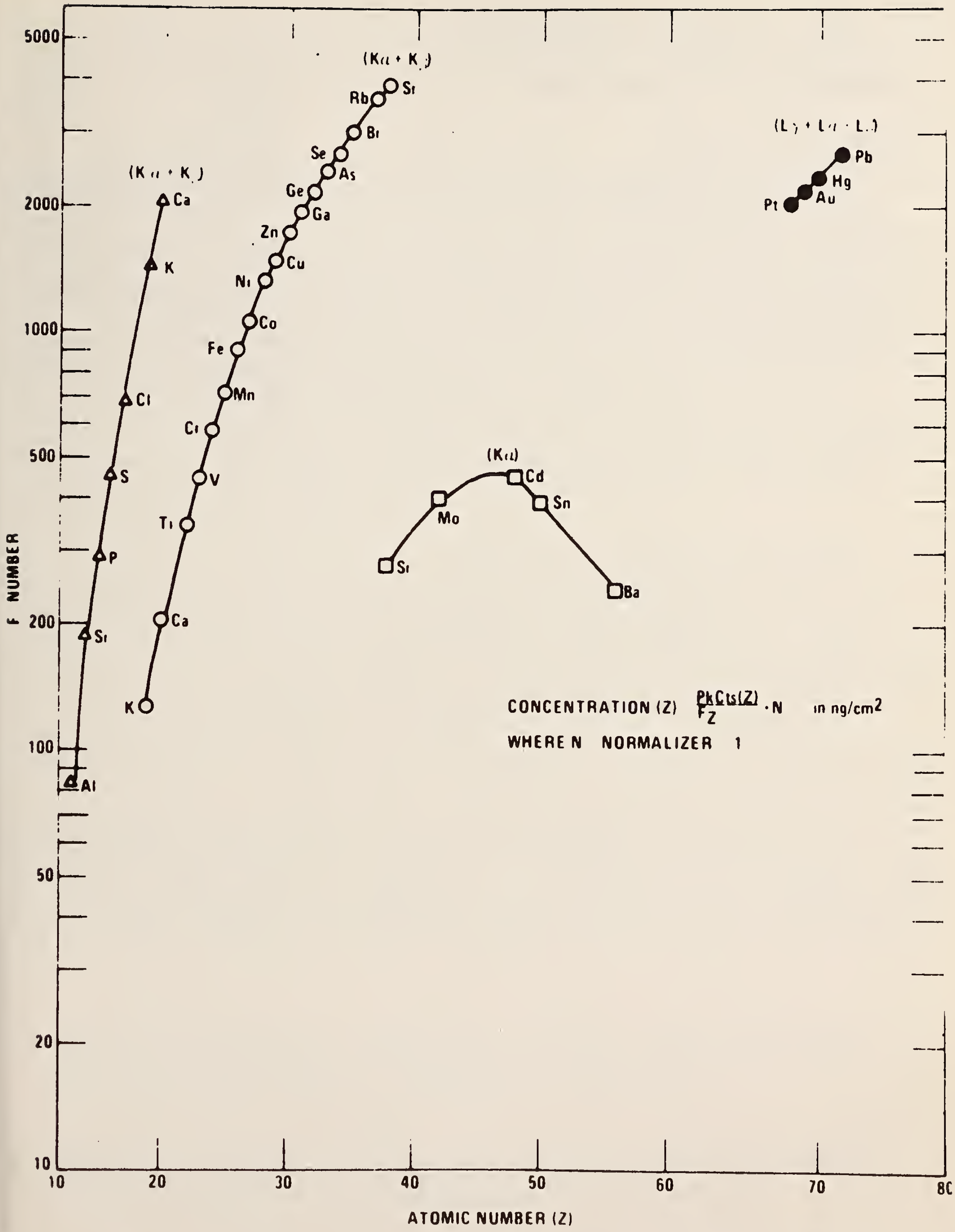


Figure 27.5 EDXRF calibration constants for Ti(△) Mo (○●) and Sm (□) secondary targets

Table 27.3
Error Analysis

1. Sample X-Y-Z Displacement	±2%,X-Y ±2%,Z
2. Anode KV-I Drift	±2%,Short τ(2σ) ±1-5%,Long τ
3. Peak Centroid Shift	±2-0%,0.1 FWHM Shift
4. Counting Statistics	±2%,10k Counts (2σ)
5. Attenuation Corrections	±1%,Calibration Standards
6. Calibration	±4%,NBS-Calibrated Elements ±6-10%, Other Elements

in uniformity, intraelemental ratios, NBS results, attenuation corrections, and 2% for the F-number determinations. The ranges of uncertainty for other elements, ± 6-10%, are estimated, and will be reviewed upon completion of the calibration study.

XRF intercomparisons were made between solution deposited standards from Columbia Scientific Industries[2] (CSI) and vacuum deposited standards from MicroMatter Company[3] (μM) for the elements S, K, Ca, Cr, Fe, Cu, Mo, Ba and Pb. Each calibration standard was analyzed three times, and a relative standard deviation for the averaged results was less than 3.5% in each case. Background subtractions were accomplished by normalizing stored blank spectra to fit regions located above the characteristic peaks. Attenuation corrections were applied to elements lighter than Fe; these are listed in Table 27.4. Figure 27.6 shows the results obtained with the expression $[I/AC]_{CSI}/[I/AC]_{\mu M}$, where I is the average number of counts in the principal characteristic peak, A is the attenuation correction, and C is the elemental concentration specified by the manufacturer.

A second XRF intercomparison was made, ratioing the same standards from CSI and μM to the vacuum deposits which had been calibrated with IDMS analyses. The procedure was identical to that used in the above intercomparison. The average ratio was 0.85 with CSI standards for the elements K, Ca, Cr, Fe, Cu, Mo and Pb. The μM standards averaged 0.88 for the same elements. A comparison between the capillary deposits and the calibrated vacuum deposits produced an average ratio of 0.97 for the elements Cr, Cu, Sr, Mo and Pb.

The systematic disagreement with both CSI and μM standards was unexpected, especially in view of a general agreement with CSI solution deposited standards reported by many laboratories in a recent round-robin study [10]. A review of the methods used in our work failed to explain a systematic error of appreciable magnitude. Indeed, the review served to increase confidence

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[2] Columbia Scientific Industries, Austin, Texas. The CSI sulfur standard had an "ultrathin" Millipore TAWP substrate. Other CSI standards used Millipore SMWP media.

[3] The MicroMatter standards intercompared with CSI and IDMS-calibrated standards were commercially prepared and were gravimetrically determined by MicroMatter Company.

Table 27.4

ATTENUATION CORRECTIONS FOR CSI AND μM STANDARDS

	A(CSI)[a]	μg/cm^2(CSI)	A(μM)	μg/cm^2(μM)[b]
S	0.77	41.10	0.91	28.0
K	0.67	5.41	0.94	43.0
Ca	0.72	35.14	0.96	56.4
Cr	0.93	33.64	0.99	74.0

[a] Columbia Scientific Industries, Austin, Texas. The CSI sulfur standard had an "ultrathin" Millipore substrate Other CSI standards used Millipore SMWP media.

[b] The MicroMatter standards intercompared with CSI and IDMS-calibrated standards were commercially prepared and were gravimetrically determined by MicroMatter Company.

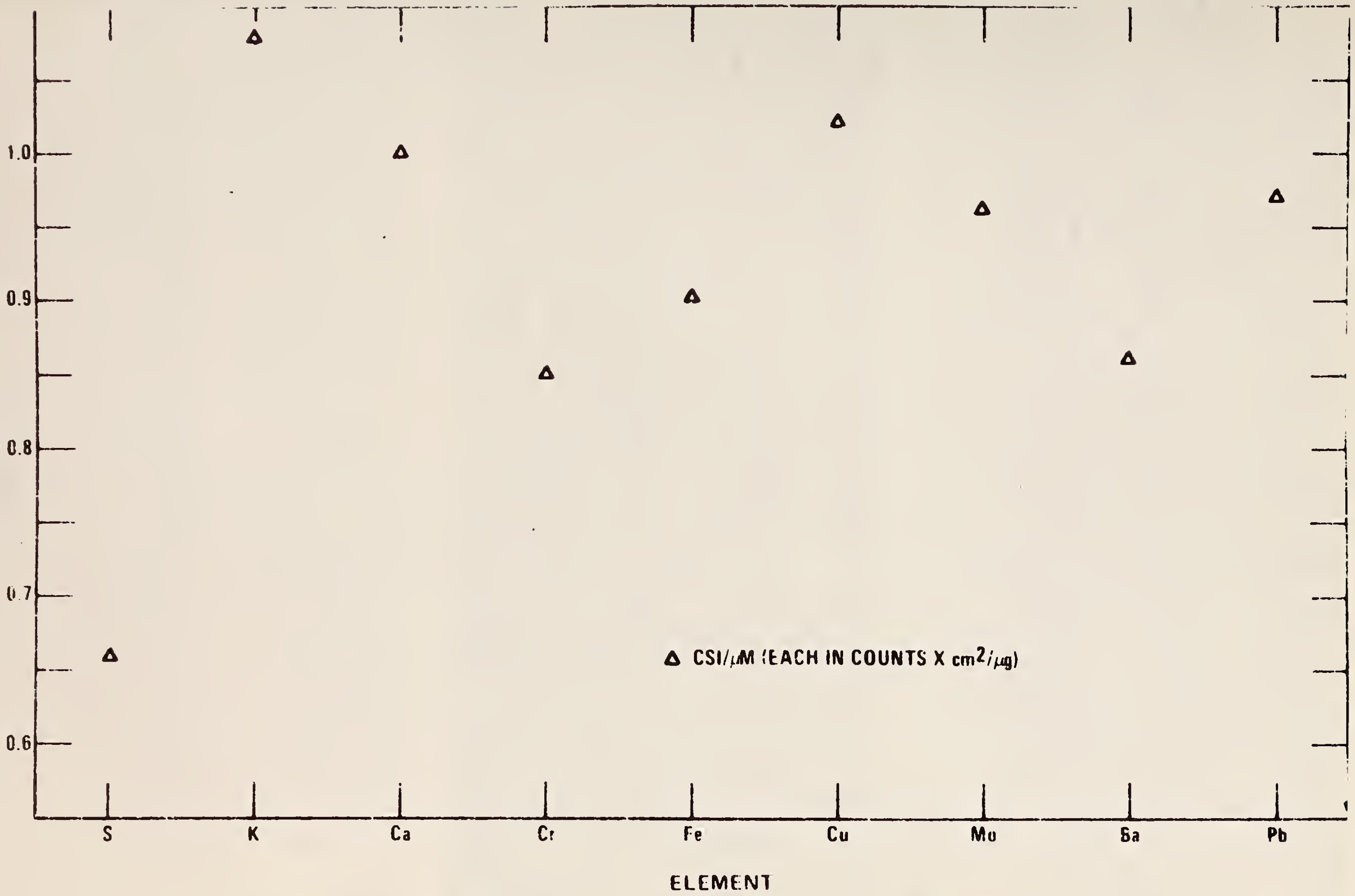

Figure 27.6 XRF comparison of CSI and μM calibration standards

in most aspects of the program. The good agreement with the capillary deposits was equally surprising, considering the relatively brief experience with that technique.

Results of preliminary vibrational tests suggest that material losses from vacuum deposits sent to the NBS might have occurred; nearly 5% of one deposit, CaF_2, and less than 1% of three other deposits were dislodged in these five-minute tests. Such losses in greater quantity could account for the kind of disparities with CSI and μM reported above. More tests are planned in order to check actual losses that occur in mailing calibration standards, particularly vacuum deposits on thin Mylar. Meanwhile, a second set of pre-ratioed and -characterized deposits will be hand carried to the NBS for analysis.

Conclusion

The comparison shown in Figure 27.6 is sufficient provocation for a concerned user of XRF spectrometry to initiate an independent calibration study. The results of this carefully planned and executed study suggest that too little attention has been paid the possibility of degradations in the accuracy of calibration standards while in shipment use and storage. The possibility that vacuum deposits undergo material losses in transit is being investigated; if losses occur, then frequent use and handling might also affect accuracy. Experience in this laboratory has shown that solution deposits, though free from mechanical losses, can be expected to lose accuracy through warping and, in some cases, to crack and tear. Thus, while obtaining an accurate calibration for an XRF spectrometer is the principal objective of this continuing effort, additional information will be sought regarding the stability of calibration standards and the validity of the intercomparisons discussed in this report.

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28. An Evaluation of Equipment and Procedures Used in the Department of Interior Respirable Coal Mine Dust Sampling Program.[1-2].

Project Leaders: Wayne A. Cassatt and Edgar S. Etz,
Analytical Chemistry Division

Objective

This work was done in response to a request from the Senate Committee on Labor and Public Welfare to "evaluate and report on the adequacy of:

(1) the approved personal dust sampling equipment used in the assessment of respirable coal mine dust concentrations in underground mines,

(2) the procedures used by the Department of the Interior (DOI) in the evaluation of the dust samples obtained under the coal mine operator's dust sampling programs, and

(3) any recent studies made by the Department or private industry concerning the coal mine dust sampling equipment."

In particular, the Bureau was requested to determine the overall accuracy of the measurement results produced under the coal mine dust sampling program as it is implemented and administered by the Mining Enforcement and Safety Administration (MESA) of the Department of the Interior. During subsequent discussions with the Senate Committee staff, the Bureau was asked to comment on the advantages and disadvantages of the area sampler concept, i.e., the use of a stationary sampling device to sample the atmospheric dust concentration in the surrounding area.

Approach

The Chairman of the Senate Committee requested that the Bureau coordinate its technical evaluation with a larger, overall study of the respirable mine dust sampling program being conducted by the General Accounting Office (GAO).

To produce the information and data needed for the technical evaluation, the NBS staff, in conjunction with members of the GAO, planned and carried out the following activities: (1) a literature survey of relevant studies conducted by other organizations, (2) personal interviews with officials, scientists and mine personnel who are participating in the mine dust program, (3) visits to coal mines, (4) examination of approved dust sampling equipment, (5) a series of sample weighing experiments performed at NBS and at program laboratories, and (6) the submission of a group of preweighed dust cassettes which were introduced as test samples into MESA's sample processing system.

The federal dust standard, enforced by MESA, calls for the dust loading in the mine atmosphere to be controlled by the mine operator such that the average concentration of the respirable fraction of this dust does not exceed 2.0 mg/m^3. This average is determined from 10 eight-hour samples collected with a personal sampler worn by a miner performing a "high risk" task in each coal mine section. The sampler consists of an air pump preceded by a fine dust filter which is in turn preceded by a cyclone separator which removes the large dust particles that ordinarily do not enter the miner's respiratory tract. The dust filter is weighed before and after sampling to yield a gravimetric measurement of the respirable dust mass. The dust concentration is calculated from this mass and the total air volume that has flowed through the filter during the collection period.

Progress

The mine visits, the weighing experiments and the submission of the test samples were undertaken by NBS scientists in cooperation with members of the GAO and the Department of the Interior.

Major Conclusions

Examinations of the personal sampler by NBS and other organizations reveal that this is a "state-of-the-art" instrument that has no proven peer in this application, but the sampler has exhibited certain important limitations during the five years that it has been utilized in the enforcement program. As of February 1975, at the end of the experimental portion of this study, one or more of the approved sampler models exhibited the following shortcomings: (1) the filter capsule lost weight while in use, (2) the air flow was difficult to adjust and maintain during use (3) the sampling head was difficult to assemble correctly and could be knocked out of alignment by physical impact (4) the actual volume of air sampled was not indicated by the instrument (5) simultaneous inversion and impact of the sampling head could contaminate the dust sample with non-respirable particles and (6) the sample could be altered without being detected. Since February 1975, the National Institute for Occupational

Safety and Health (NIOSH), who is responsible for the approval of these samplers, has taken remedial action which NIOSH officials believe will correct difficulties (1) and (3) in this list. Since that time MESA has awarded R&D contracts to various organizations to develop sample air volume indicators and to design filter cassettes which are tamper proof.

The sample weighing process, as administered today by MESA, yields an uncertainty in a particular dust mass determination that is represented by a standard deviation of 0.14 mg/m^3 which is equivalent to 7 percent at a dust concentration of 2.0 mg/m^3. The air flow rate in the sampler can be adjusted with a 5 percent precision when care is exercised. When operated in the laboratory the sampler has yielded a precision on the order of 7 percent as evidenced by a standard deviation of 0.14 mg/m^3 at the compliance level. The in-mine studies conducted by other organizations show that trained scientists, experienced in analytical measurement work, can achieve dust concentration measurement results with uncertainties ranging from 7 to 50 percent which are equivalent to standard deviations of 0.14 to 1.0 mg/m^3 at 2.0 mg/m^3. The smaller uncertainties were achieved when these scientists exercised the most meticulous care and supervision of the instruments during measurement. An analysis of these uncertainties has provided a basis to estimate that when trained analysts conduct the sampling and report the result as the mean of the measurements obtained from 10 samples, this mean will lie within 20 percent (0.39 mg/m^3 at the compliance level of 2.0 mg/m^3) of the "true" mean with 95 percent probability. The uncertainty to be expected in the normal program operations, i.e.,when the miners and mine operators perform and supervise the sampling and when the weighings are made in the normal manner, is estimated to be as large as 31 percent or 0.63 mg/m^3.

The personal dust sampling equipment currently used in the MESA program appears amenable to a number of improvements which would be expected to reduce each of the errors identified above to a significant degree, but this remains to be demonstrated. The more important improvements should come from redesign of the filter cassettes, one of the filter capsules and the air flow meters.

The total reported experience with area samplers is insufficient to provide NBS scientists with a sound basis for a final assessment of this device. The area sampler does appear to offer several advantages which suggest that it may be a desirable complement to the personal dust sampler, but again this remains to be demonstrated.

References

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29. X-Ray Fluorescence Analysis of Air Particulates

Project Leader: K. F. J. Heinrich, Analytical Chemistry Division
Other Personnel: R. L. Myklebust, M. M. Darr, P. A. Pella

Objective

This work was undertaken in order to evaluate the relative merits of several configurations of both dispersive and non-dispersive x-ray fluorescence analyzers with respect to their applicability to the analysis of airborne particulates collected on filter paper.

Approach

Recent advances in Si(Li) solid-state detectors used in energy dispersive x-ray analysis have improved their resolution and sensitivity to an extent that the analysis of air particulates on filter paper is now possible. These advances have provided competition for the previously existing technology of x-ray spectrometry using wavelength dispersion by crystal monochromators. However, developments in each of these areas have made uncertain the relative merits of each arrangement in terms of sensitivity, accuracy, economy and ease of use. The results of this project will provide data that will allow rational decisions to be made regarding the choice of a most suitable configuration.

Progress

We have selected two instrumental arrangements for experimental testing. The data thus far produced should serve as a guide to the choice of configuration of apparatus most appropriate for the analysis of airborne particulates.

In the energy dispersive arrangement, we have been able to produce effective excitation of the x-ray lines of interest while minimizing background radiation. An apparatus was constructed which uses an x-ray tube to generate characteristic x-rays from a secondary target which excite the specimen (See Figure 29.1.). This secondary target reduces the scattering of polychromatic bremsstrahlung radiation generated in the x-ray tube, thus reducing the background level. Detection is accomplished by means of a Si(Li) solid-state detector and multichannel pulse height analyzer.

The wavelength dispersive apparatus is a commercial, single-channel x-ray spectrometer which uses crystal monochromators. The x-ray tube, crystal, and detector can be selected to produce the most efficient excitation and the optimum x-ray signal to background ratio for the element being measured.

A preliminary comparison of the two methods was made using NBS Standard Reference Material (SRM) 1571 Orchard Leaves. This powdered material is well characterized for some of the elements of interest to air pollution studies, such as copper, zinc, and lead. The initial tests indicated that the elements lying between manganese and lead in the periodic table can be detected at levels of 1 to 3 ppm when using the wavelength dispersive method. For energy dispersive x-ray analysis, similar detection levels have been reached when the appropriate conditions are properly selected.

In order to perform quantitiative analyses of air particulates on filter paper, standards must be available which consist of known amounts of a well-characterized particulate material distributed on filter paper. Such standards have been prepared for obtaining calibration curves for iron and manganese by filtering from liquid suspension Standard Reference Material cements, glasses, iron oxide and manganese oxide and depositing these materials on membrane filters. About 900 μg of material per cm^2 of filter paper was deposited in each case. The iron calibration curve obtained with the wavelength dispersive system is shown in Figure 29.2 (up to 30 $\mu g/cm^2$ of Fe) and in Figure 29.3 (same curve extended to 300$\mu g/cm^2$ of Fe). The data all fall on the same straight line; therefore, for these specimens, neither the particle size nor the matrix material have any significant effect. The data for manganese are also in agreement with these results.

Some real air particulates collected on filter papers have been analyzed for iron and manganese. These samples were obtained from Columbia Scientific Industries and are being used for inter-laboratory comparisons. Our iron and manganese determinations will be sent to Columbia Scientific; however, their results are not yet available.

Preliminary work with the energy dispersive system indicated several possible changes that might be made for improving the sensitivity and stability of the system. These changes have recently been made and the quantitative tests using the iron and manganese standards will be repeated with the improved energy dispersive instrument.

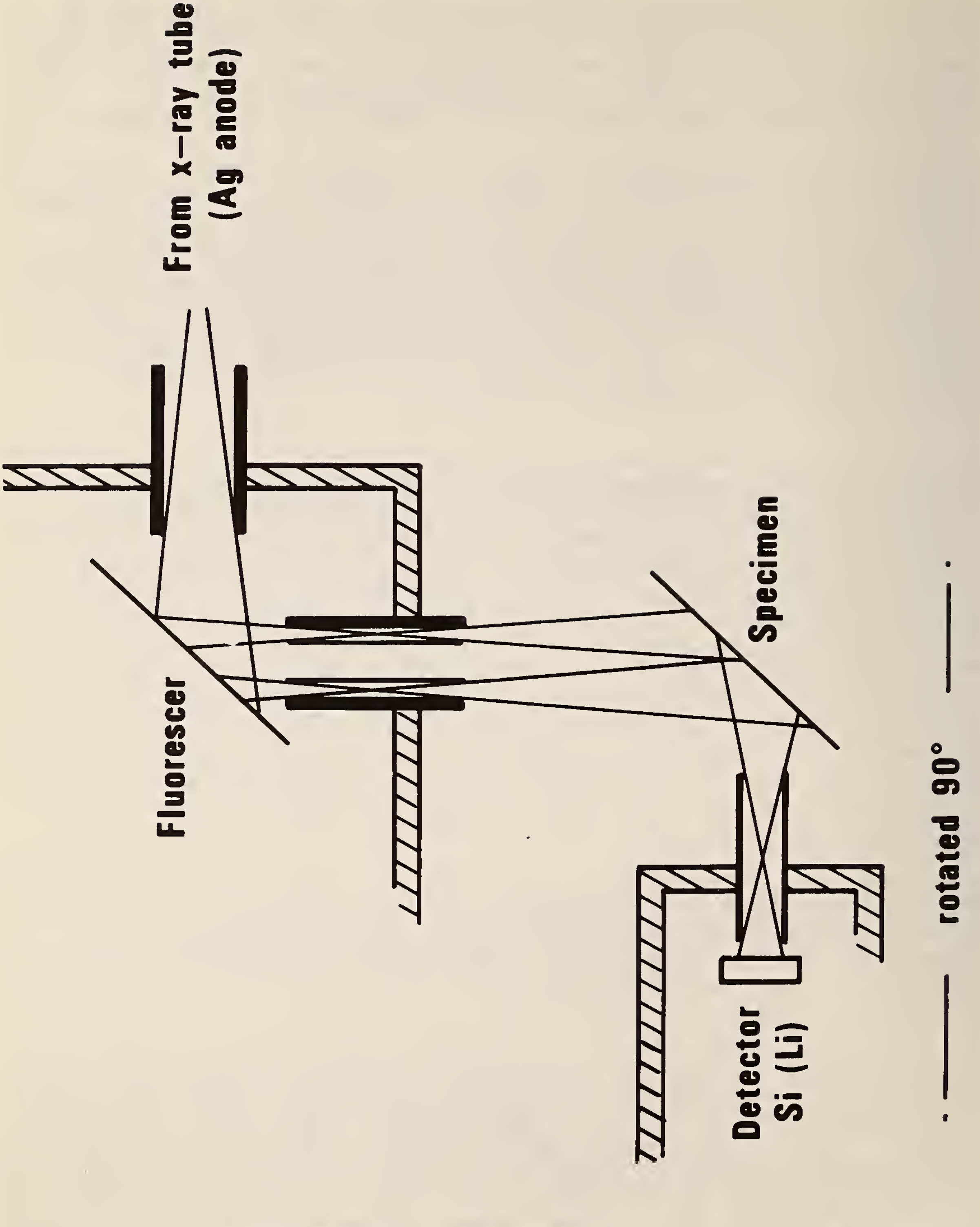


Figure 29.1 NBS Energy-dispersive (non-diffractive) x-ray fluorescence apparatus

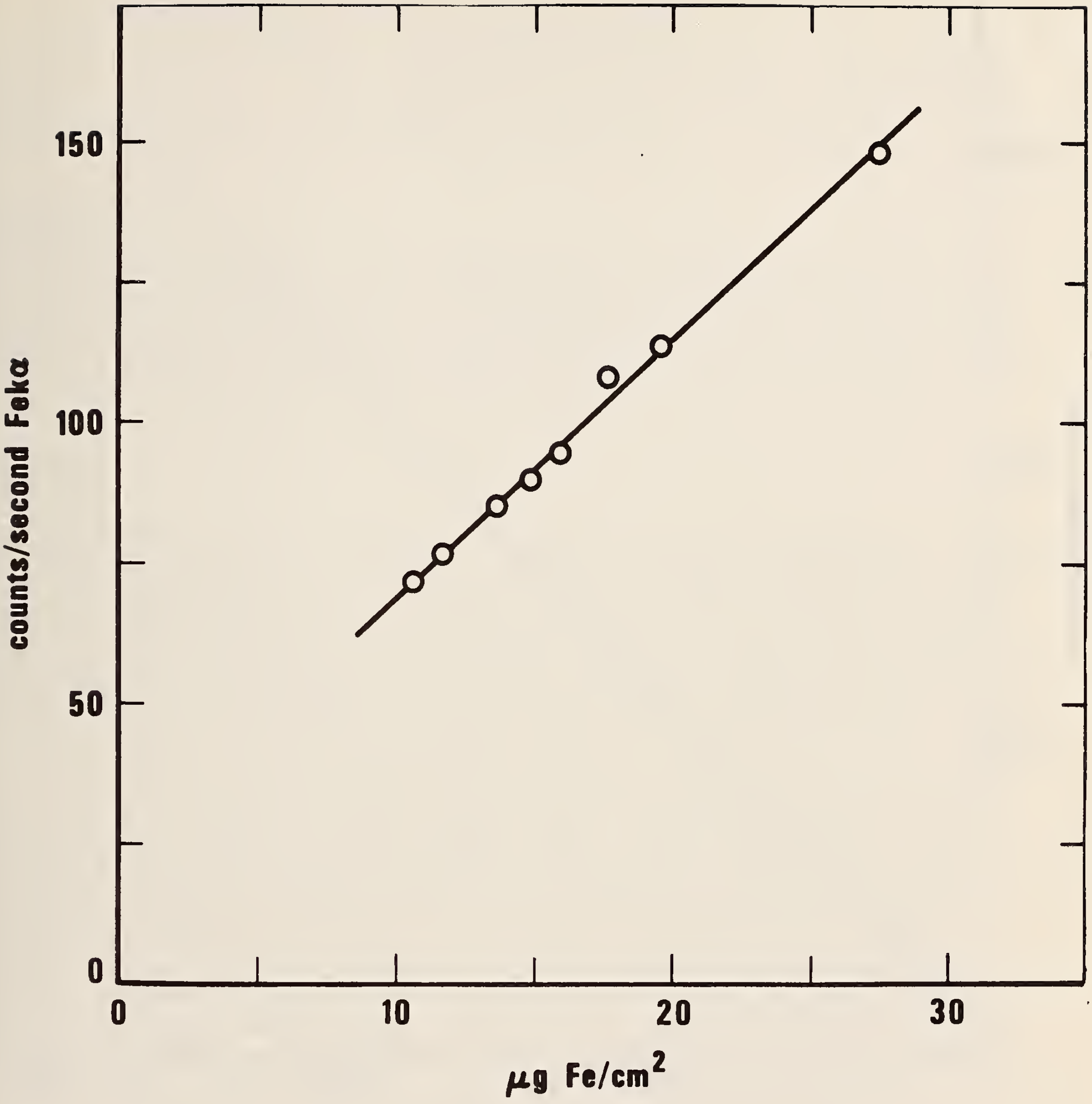


Figure 29.2 Iron intensity from filter paper standards versus iron concentration

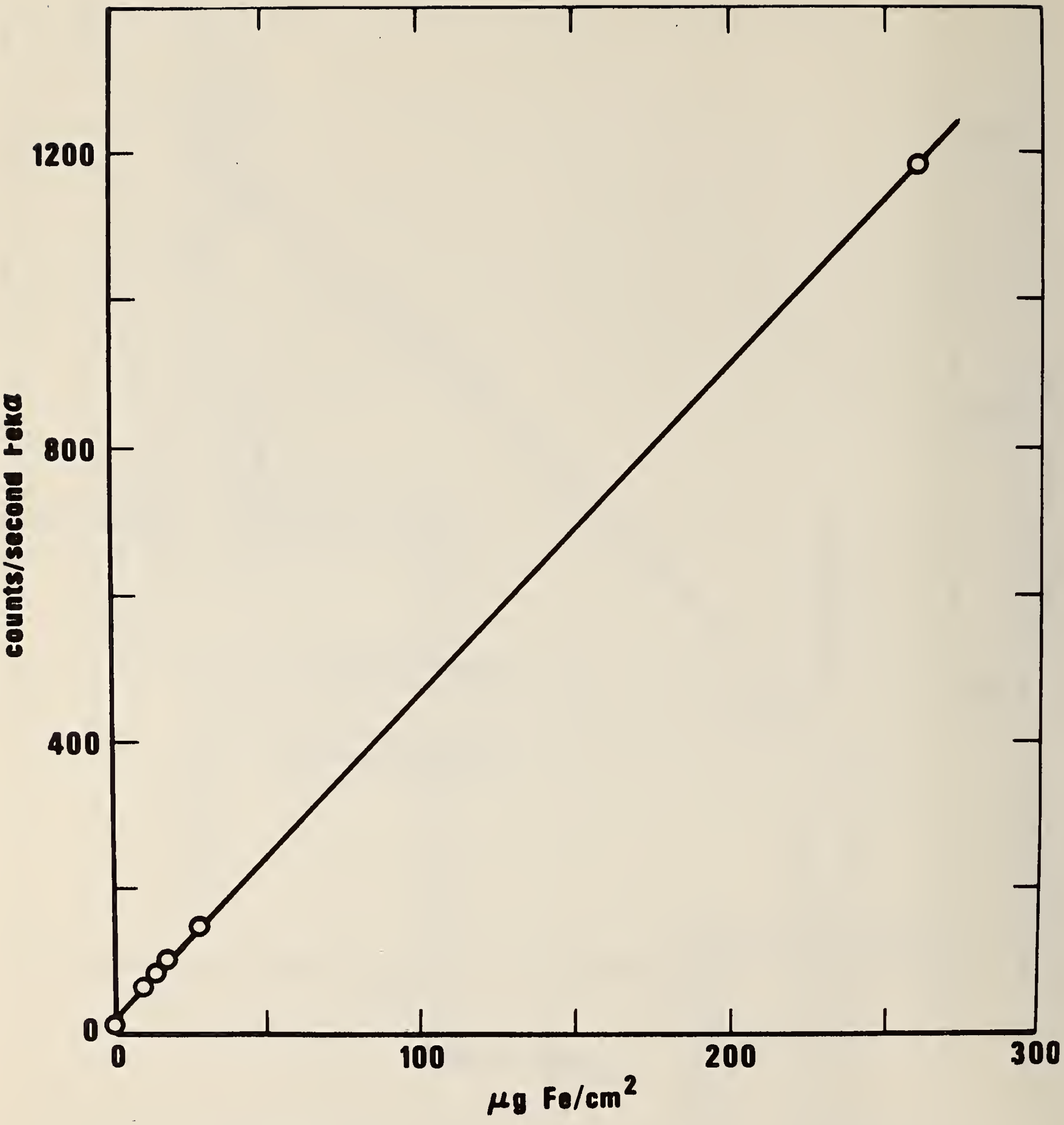


Figure 29.3 Iron intensity from filter paper standards versus iron concentration (curve extended to 300 μg/cm³ of Fe

30. Instrumentation for Particle Sizing

Project Leader: M. L. Greenough, Measurement Engineering Division
Other Personnel: J. Cohen, R. Frisch, E. C. Palasky

Objective

Instrumentation is being developed for determining the size of particles in the 0.1 to 5 micrometer diameter range, based upon the selective forward scattering of a light beam across which the particles are caused to flow. The instrument development was funded by the Environmental Protection Agency.

Approach

The general approach follows that was proposed and experimentally verified by Dr. C. C. Gravatt of NBS, Polymer Division. Specifically the goal is to detect the light scattered in narrow conical bands located at 5 degrees and at 10 degrees from the beam axis. The ratio of the light levels in the two bands is extracted for individual particles during transit. These ratio indications are summed in a small computer for periodic printout of numeric distribution according to particle size.

The system is built around an argon ion laser whose beam is focused as it enters the sample cell. The air sample being measured is passed through the cell, after being extracted from an overall intake manifold. When particles contained in the air pass through the narrow laser beam, the small amount of scattered light is transmitted through a conical mask assembly called the director, to two photomultiplier tubes. These tubes are the sources of analog signal pulses whose relative amplitudes during coincidence are predicted to be dependent upon size of the particle initiating the scattering. Detection is in two conical bands each one degree wide, at 5 and 10 degrees from the beam axis.

The pulse signals are fed to an interface unit providing the interconnection between the optical signals and the computer. In the interface the 5-degree signal is applied to 32 threshold comparison circuits which have appropriate voltage dividers. To the other side of the comparison circuits is applied the 10-degree signal. Whenever the 10-degree signal exceeds the threshold fraction of the 5-degree signal, a digital output is created. The output of the 32 comparison circuits is to be recoded in a computer word developed on the basis of one eight-bit byte for each discrete particle which is detected. Thus eight bits in the word convey the information regarding particle size. At the end of the pulse time this work is transmitted out of the interface buffer to be accumulated in the computer's memory according to bit contents.

At periodic intervals, perhaps five minutes or as desired, the computer will print out a report giving the distribution of accumulated particle sizes, using the teletype unit which is to be a part of the computer system.

Progress

The instrument was completed and made ready for delivery to its sponsor, the Environmental Protection Agency. The major phases of activity were:

1) Mechanical Design and Construction

   The various components were mounted into the 115-centimeter (45-inch) high rack cabinet. This included the computer, electronic signal-processing circuits, computer interface, laser power supply, other power supplies and the vacuum pump. The optical assembly at the top of the cabinet comprises the laser, sensing head photomultiplier tubes and flowmeter. With an additional teletype unit associated with the computer, the complete system weighs approximately 125 kilograms (275 pounds).

2) Computer Program Preparation

   Documentation supplied by the manufacturer of the computer was found to be limited for a machine of this small (4k words) size. Consequently it was necessary to prepare several utility programs in the beginning. The operating program was written with the aid of a remote-terminal editor system, followed by steps of manual and machine translation to produce the working paper tape program. In operation, printouts of the distribution of detected particulates are made at intervals under the control of the operator. The printout shows the accumulated contents of each ratio category, for example 10 to 13 percent, 13 to 16, and so on. These output data may then be plotted to furnish graphic indication. Approximately 20 percent of the machine memory capacity is used by the operating program, leaving considerable room for later expansion if desired.

3) Testing, Operational Experience

In trial operation a few modifications were found necessary. One of these was the optical calibrator which enables setting of the gains for the two phototubes. The fine-wire arrangement originally planned proved to be too critical in positioning. It was replaced with new yoke carrying an optical diffuser and a neutral density filter. When the yoke is extended into position, the laser beam is attenuated and scattered approximately uniformly, reaching both the phototubes. Gain adjustment is then accomplished by varying the supply voltage on each phototube until its output signal reaches a designated value. Retraction of the yoke then permits normal action.

Additional provisions for operational verification allow the electrical insertion of dummy signal ratios obtained from a test panel control. With this technique the ratio-determining circuits we found capable of a dynamic signal range of 100 to 1 with no more than one step (3%) error. Although this is a wide range, there is a possibility than an even larger one may be needed to cope with the desired span of particle size. More operational experience should show whether recalibration will be necessary to cover the extremes of particle size, or whether the present 100X dynamic range is sufficient.

One of the extrapolations from the original experiments was a prediction that a low-power laser should be adequate for the system, in view of certain optical changes introduced in the design. This assumption proved justified; the signal levels were such that the laser could be operated at half power or less, increasing its useful life.

Polylatex spheres of several sizes in the range of 0.3 to 3 micrometers were introduced into the inlet port and the resultant distribution of ratios noted. Although it is too early to say what the ultimate discriminatory ability of the system will be, the preliminary results are quite promising. In order to quantify the particles used so far, electron microscope images have been produced and examined. The particles have been noticeably egg-shaped, which is entirely in keeping with the asymmetrical characteristic noted in the indicated distribution.

The instrument was delivered along with requisite documentation to the Environmental Protection Agency.

31. X-Ray Analysis of Limestone Scrubber Slurry

Project Leader: A. Perloff, Inorganic Materials Division

Objective

If good quantitative analyses of the material is desired the x-ray technique is not the answer. Without adding known amounts of an internal standard an estimate of each of the major components can be crudely obtained if that component represents less than approximately 50% of the mixture. Such an estimate would have a large associated error, i.e., an estimate of 30% should be taken as meaning the amount of that component probably lies between 20%-40% of the mixture. The use of an internal standard would probably reduce this error range by a factor of 2. Recourse to orthodox wet chemical procedures would be necessary if greater accuracy is required.

Approach

It was hoped that peak intensities or relative peak intensities of the major components of the mixture might provide an adequate measure of the composition provided constant conditions of the diffractometer, sample holder and sample packing could be maintained. This would eliminate the necessity for sample weighings and the possibility of errors from inadequate or uneven mixing which could arise from the use of an internal standard.

If this procedure was not satisfactory the use of an internal standard could be estimated from mixtures containing a constant amount of one component.

Progress

The diffraction pattern of limestone scrubber solids was analyzed. It was established that all of the distinct peaks could be accounted for on the assumption of a mixture of three components: $CaCO_3$ (calcite form), $CaSO_3 \cdot \frac{1}{2}H_2O$, and $CaSO_4 \cdot 2H_2O$. Pure samples of these compounds were purchased or made for x-ray examination and as stock material for making up mixtures of known composition. The mixture compositions are listed in Table 31.1 and the observed net peak heights (total peak height minus background) are given in Table 31.2. Intensity measurements were made on samples which had been mixed and ground for 5-10 minutes in a mullite mortar and pestle, loaded loosely into the holder (Figure 31.1) and compacted by tapping the holder until the top surface appears smooth and uniform.

TABLE 31.1

SAMPLE COMPOSITIONS

	$CaSO_3 \cdot \frac{1}{2}H_2O$		$CaCO_3$		$CaSO_4 \cdot 2H_2O$	
Mixture	mg	%	mg	%	mg	%
1	198.25	50.40	164.64	41.85	30.49	7.75
2	100.64	25.80	202.96	52.03	86.45	22.16
3	182.13	43.84	87.30	21.01	146.00	35.14
4	148.52	33.62	148.03	33.51	145.21	32.87
5	144.44	36.47	164.50	41.54	87.08	21.99
6	187.18	46.39	142.07	35.21	74.20	18.39
7	247.92	56.86	144.59	33.16	43.47	9.97
8	96.87	20.08	159.71	33.11	225.72	46.80
9	44.35	10.15	144.87	33.15	247.78	56.70
10	314.98	69.98	90.05	20.01	45.05	10.01
11	270.06	60.01	90.06	20.01	89.89	19.98
12	157.59	34.99	90.31	20.05	202.52	44.96
13	89.96	19.96	90.53	20.08	270.26	59.96
14	44.93	9.99	89.87	19.98	315.01	70.03
15	90.11	20.02	188.94	41.99	170.95	37.99
16	44.98	10.00	188.99	42.00	216.01	48.00
17	360.03	79.99	45.03	10.00	45.04	10.01
18	292.50	64.99	45.04	10.01	112.50	25.00
19	225.00	49.99	45.05	10.01	180.04	40.00
20	157.52	35.01	44.97	9.99	247.48	55.00
21	90.05	20.01	45.02	10.00	315.04	69.99
22	44.98	10.00	45.01	10.00	359.99	80.00

TABLE 31.2

Observed Net Peak Heights

Peak #							
Sample #	1	2	3	4	5	6	7
1	0.90	1.62	0.96	0.78	2.97	---	8.45
1*	1.10	1.77	0.82	0.61	2.55	---	8.05
2	1.96	0.77	0.39	1.45	1.44	0.8	10.8
3	3.30	1.25	0.75	2.41	2.55	1.85	4.63
3a	3.28	1.31	0.66	2.33	2.62	1.70	4.45
4	2.60	1.12	0.74	1.85	1.80	0.7	7.00
4a	2.46	1.09	0.80	2.07	1.88	1.0	7.21
4*	1.55	1.40	0.50	1.48	1.60	0.70	6.33
4a*	1.67	1.26	0.46	1.52	1.70	0.75	6.26
5	1.83	1.36	0.85	1.32	2.10	0.73	8.02
6	1.50	1.73	0.68	1.18	3.17	0.50	7.15
6a	1.52	1.58	0.69	1.13	3.07	0.60	7.31
7	1.13	1.70	0.97	0.86	2.81	---	7.00
8	4.70	0.80	0.42	3.32	1.02	1.90	7.40
9	5.84	0.36	0.31	4.14	0.88	2.65	7.18
10	0.6	2.28	1.50	0.53	3.37	---	4.00
11	1.40	1.83	0.85	1.02	3.41	0.75	3.86
12	5.30	1.50	0.74	3.34	1.90	2.17	5.17
13	5.57	0.62	0.32	4.49	1.20	3.07	4.43
14	8.90	0.55	0.25	5.54	0.63	4.13	4.85
15	2.50	0.80	0.30	1.70	1.00	0.8	9.05
15a	2.15	0.80	0.27	1.72	1.08	0.9	9.18
15*	2.55	0.62	0.33	1.72	1.15	1.0	8.35
16	3.83	0.4	0.2	2.70	0.68	1.75	9.18
17	0.43	2.42	0.95	0.35	3.49	---	1.70
18	1.92	2.02	1.22	1.25	3.42	1.10	2.30
19	2.81	1.72	0.95	2.27	2.77	1.60	2.48
20	4.53	1.00	0.62	4.02	2.10	2.50	2.25
20*	2.37	1.87	0.55	2.45	1.85	1.67	2.32
21	5.00	0.82	0.40	4.94	1.24	3.03	2.43
22	6.02	0.30	0.20	5.50	0.73	3.57	2.31

TABLE 31.2 (continued)

a = Pattern rerun with same sample and same packing.

* = Pattern run after regrinding and repacking

Peak 1 is $CaSO_4 \cdot 2H_2O$ line at d = 7.56

Peak 2 is $CaSO_3 \cdot \frac{1}{2}H_2O$ line at d = 5.55

Peak 3 is $CaSO_3 \cdot \frac{1}{2}H_2O$ line at d = 5.33

Peak 4 is $CaSO_4 \cdot 2H_2O$ line at d = 4.27

Peak 5 is $CaSO_3 \cdot \frac{1}{2}H_2O$ line at d = 3.14

Peak 6 is $CaSO_4 \cdot 2H_2O$ line at d = 3.06

Peak 7 is $CaCO_3$ (calcite) line at d = 3.04

TABLE 31.3

Data for Constant Carbonate Composition Curves

Sample #	% sulfite	$\frac{\text{sulfite}}{\text{carbonate}}\left(\frac{\text{Pk 4}}{\text{Pk 7}}\right)$	% sulfate	$\frac{\text{sulfate}}{\text{carbonate}}\left(\frac{\text{Pk 4}}{\text{Pk 7}}\right)$
10% calcite				
22	10	0.316	80	2.381
21	20	0.510	70	2.033
20	35	0.934	55	1.786, 1.056
19	50	1.117	40	0.915
18	65	1.486	25	0.543
17	80	2.053	10	0.206
20% calcite				
14	10	0.130	70	1.143
13	20	0.271	60	1.013
12	35	0.368	45	0.646
3	44	0.571	35	0.522
11	60	0.883	20	0.264
10	70	0.842	10	0.132
33-35% calcite				
9	10	0.123	57	0.577
8	20	0.138	47	0.449
4	33	0.260	33	0.264-0.287, 0.234-0.243
6	46	0.431	18	0.155-0.165
7	57	0.401	10	0.123
∿ 42% calcite				
16	10	.074	48	0.294
15	20	0.110-0.118, 0.138	38	0.188, 0.206
5	36.5	0.262	22	0.165
1	50	0.351	8	0.092-0.076

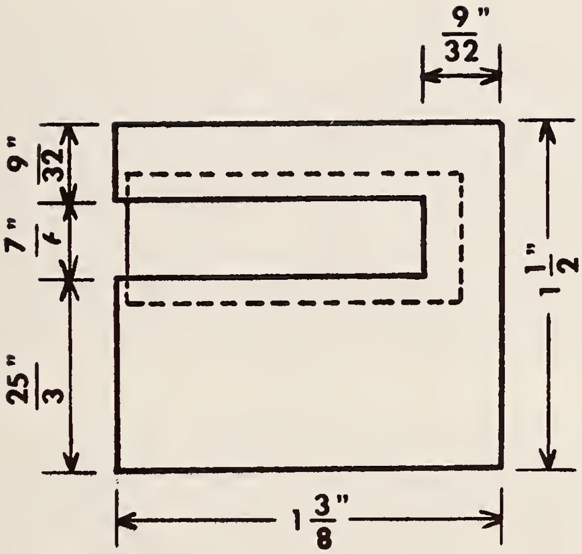


Figure 31.1

Sample holder is cut from 1/16" Aℓ plate. The dashed lines represent a glass slide cemented to the bottom. When loading a sample, a second glass slide is clamped on the top surface. The sample is introduced from the open end. While holding the open end upright the holder is tapped with a metal rod to compact the sample. The second slide is removed before placing the holder on the diffractometer.

The samples cannot be pressed to give a good surface because this results in highly oriented diffraction patterns. The relative intensity of the $CaSO_3 \cdot \frac{1}{2} H_2O$ peaks at d=5.55 and d=5.33 was used as a guide to decide whether the samples were free of marked orientation effects. In an oriented sample the 5.33Å peak becomes the strongest line and may be an order of magnitude greater than the 5.55Å peak. With a calcium sulfite sample free from preferred orientation the peak at d=3.14Å is the strongest and the 5.55Å peak is roughly twice the intensity of the 5.33Å peak.

All patterns were made with the same holder, diffraction unit and experimental conditions. This is absolutely necessary as an x-ray diffraction calibration curve is only valid when all experimental conditions and equipment are held constant. The patterns were made on a Philips diffractometer with Ni-filtered Cu radiation. A scintillation detector, pulse height analyzer and strip charter recorder were used. The slit system consisted of 1° divergent and receiving slits coupled with 0.006" limiting slit. Peak heights and backgrounds were measured on the strip chart record. A scanning speed of 1/2 degrees 2θ per minute and a time constant of 1/2 seconds were used.

For each pattern the relative peak heights of seven peaks were measured; one calcite peak (d=3.04Å), three sulfite peaks (d=5.55Å, 5.33Å and 3.14Å) and three sulfate peaks (d=7.56Å, 4.27Å and 3.06Å). The strongest peaks for calcite (d=3.04Å) and the sulfite compound (d=3.14Å) were used as a measure of their proportions. It was felt that the second strongest line (d=4.27Å) for the sulfate salt would be a better criterion than the low angle strongest peak (d=7.56Å). At the lower angle the area intercepting the x-ray beam is larger than the sample area and it becomes harder to maintain a reproducible amount of sample in the beam.

Results and Conclusions

The graphs of Figures 31.2 and 31.3 indicate that, within crude limits of accuracy, the peak heights of the major peak of each component can give an estimate of the percentage of that component as long as it is less than approximately 50% of the total mixture. The confidence that could be placed in such an estimate varies with each compound. The carbonate is best in this respect. This is due to the much steeper slope of the curve and to the fact that it is not very prone to preferred orientation because the starting material was already in a finely powdered form.

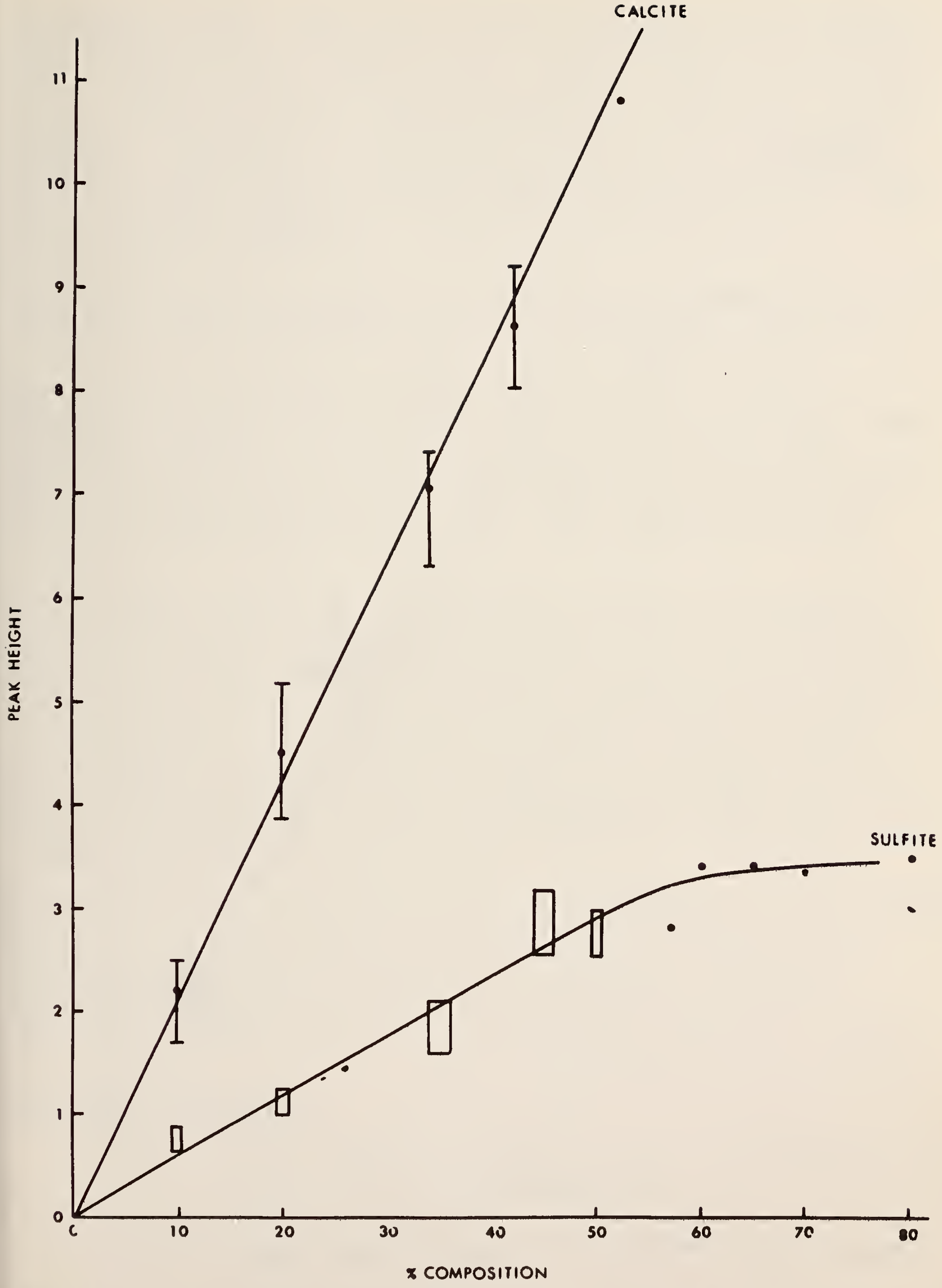


Figure 31.2 Calcite and sulfite peaks vs. composition

Figure 31.3 Sulfate peak heights vs. composition.

The sulfite curve appears to be next in terms of accuracy and reproducibility. It is much less accurate than the carbonate curve because of the lower slope. The influence of preferred orientation is probably less in the sulfite pattern compared to the sulfate pattern because the sulfite lines were used to decide if orientation effects were present. It is highly possible, especially in mixtures high in sulfate and low in sulfite, that a pattern could be obtained in which the sulfite was essentially unoriented and the sulfate was still preferentially oriented.

The sulfate curve is the worst in terms of reproducibility and accuracy. This is probably due to orientation effects not being controlled as well as for the sulfite compound.

The use of an internal standard would improve matters slightly as illustrated by the constant carbonate composition curves of Figures 31.4 and 31.5. The results could be improved further by the choice of a more appropriate internal standard which could give a steeper, more sensitive curve. Averaging several measurements for each composition would improve the accuracy.

The use of an internal standard would require two weighings and thorough mixing for each sample you wish to analyze. Weighing, mixing, grinding and a single scan would take from 30-60 minutes per sample. Additional grinding, mixing and scans, which would be necessary if more confidence is required in the results, could take about 30 minutes each. The end result would be semiquantitative at best. I do not know what present wet chemical techniques are available for this specific problem, but I would be surprised if there were not some relatively rapid titrimetric techniques which could give better results in a shorter time.

Whether the x-ray technique can be used depends on your ultimate objective. If monitoring the quantity of calcite is the primary objective then it can be used effectively with an appropriate internal standard with the time requirements reduced by scanning only the area of interest. If it is important to know the relative amounts of sulfite and sulfate salts with good accuracy, I would not recommend the technique.

Materials Preparation

$CaCO_3$ - B and A reagent grade powder. X-ray pattern shows only the calcite phase.

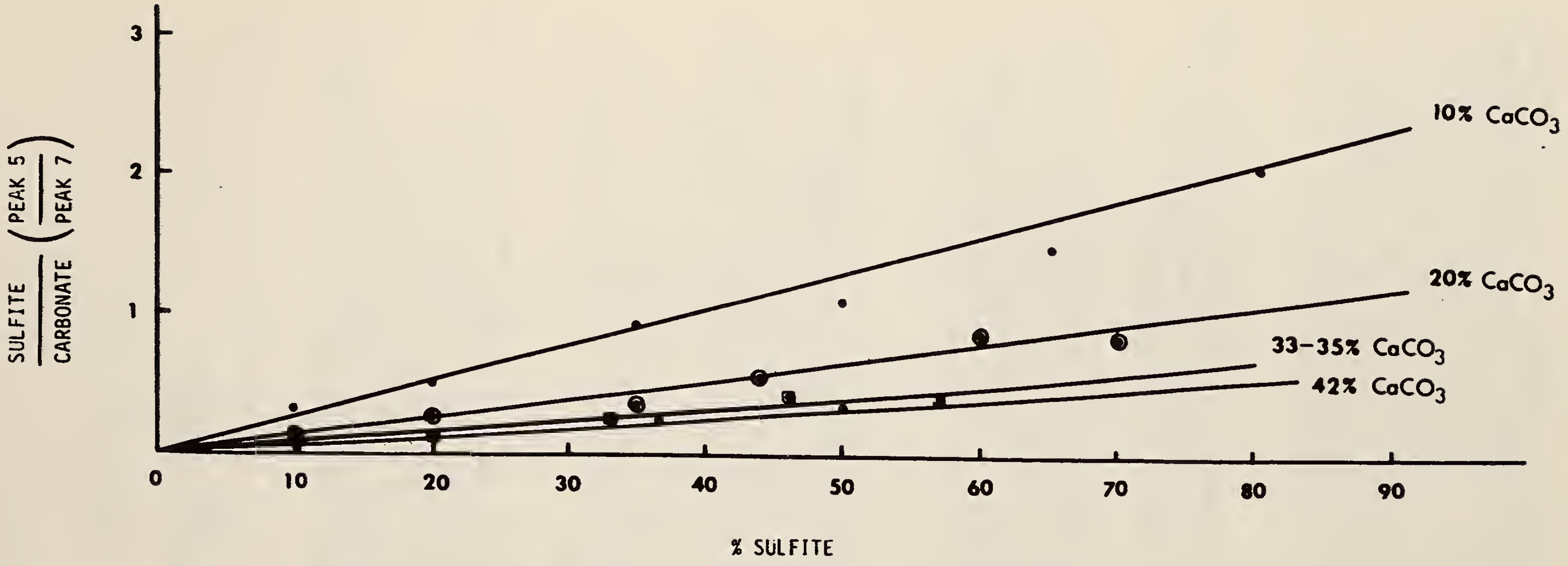


Figure 31.4 Ratio of sulfite to carbonate peak heights vs. % sulfite.

- ● 10% carbonate,
- ⊙ 20% carbonate,
- ▣ 33-35% carbonate,
- ◬ 42% carbonate.

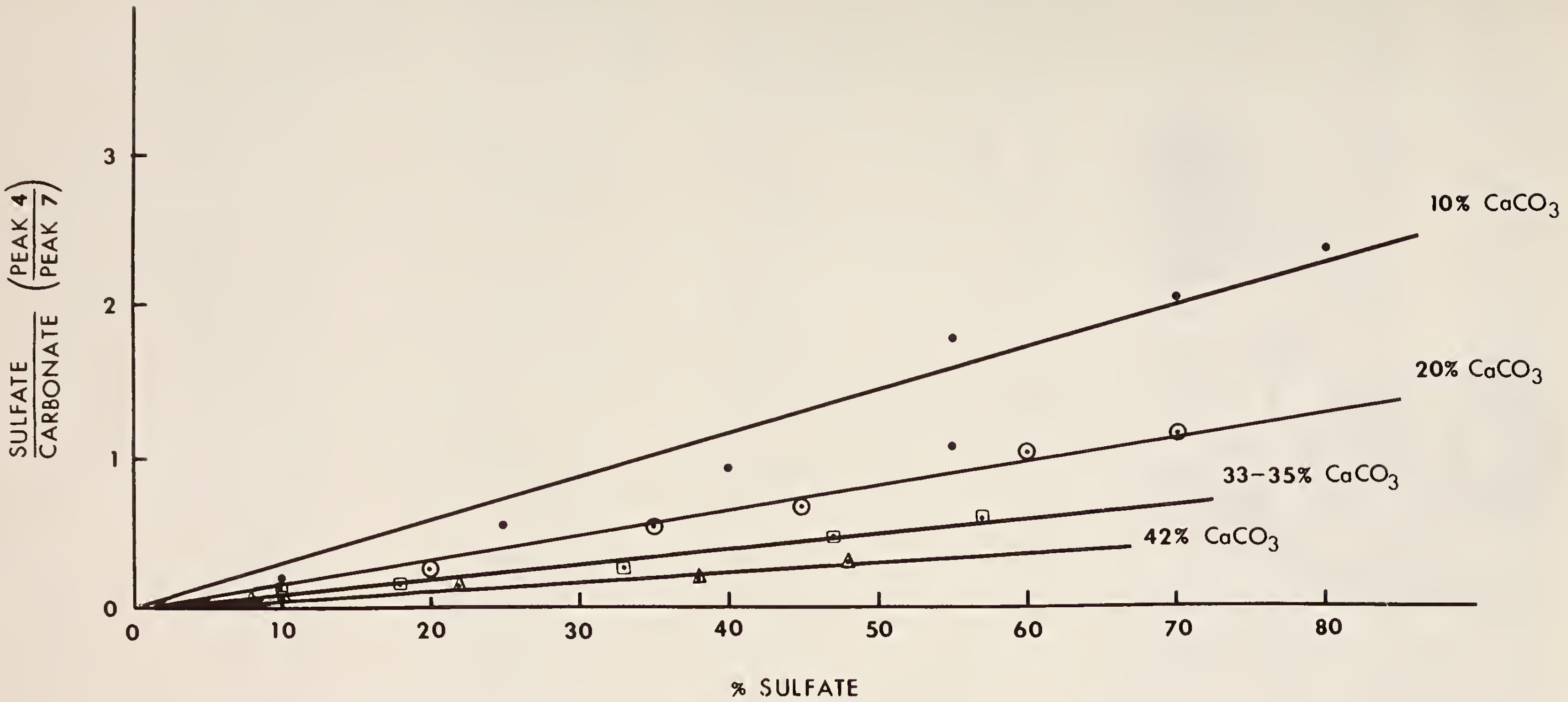


Figure 31.5 Ratio of sulfate to carbonate peak heights vs. % sulfate.

● 10% carbonate,

⊙ 20% carbonate,

⊡ 33-35% carbonate,

△ 42% carbonate.

$CaSO_4 \cdot 2H_2O$ - Precipitated by combining solutions of reagent grade $Ca(OH)_2$ and Na_2SO_4. A well crystallized single-phase product is obtained by digesting overnight.

$CaSO_3 \cdot \frac{1}{2}H_2O$ - A well crystallized product is obtained by slow diffusion of solutions of $CaCl_2 \cdot 2H_2O$ and Na_2SO_3. A substantial yield of the product requires about three weeks to form. Rapid precipitation produces a poorly crystallized product which is low in calcium. This suggests that there may be an amorphous form of a higher hydrate which is metastable.

32. Particle Size by Light Scattering

Project Leader: Ilan Chabay

Objective

The primary goal of this project has been to design, fabricate, and assemble the components of a laser scattering system for the measurement of particle size distributions.

Approach

Light scattered by a particle falling in a gravitational field exhibits a Doppler shift, the magnitude of which is determined by the velocity of the particle which, in turn, depends upon its size, density and the medium through which it falls. This Doppler shift is to be measured to assess the particle size.

Progress

The equipment includes an argon ion laser, an etalon, an air supported optical table (which provides vibrational isolation), a set of optical components with adjustable mounts, a photomultiplier tube, PMT housing and PMT power supply, a signal correlator and a digital voltmeter.

In order to introduce the particles into the scattering region under well-defined conditions, a wind tunnel was designed and constructed. It is designed to create a uniform velocity, slow air flow in the scattering region through which the particles fall. The velocity due to the settling motion of the particles can then be unequivocally separated from the mass flow velocity of the surrounding air.

An optical bench, on which the detection apparatus is mounted, was built. It allows the angle of scattering to be chosen and changed readily and with high precision.

Preliminary tests done with water droplets from a simple atomizer served to indicate that the optics and correlator were set up and operating correctly.

The interfacing and software for direct computer processing of the data gathered by the correlator is being designed. This will involve taking data from the correlator as an autocorrelation function, performing a fast Fourier transform, determining the sizes of particles present from Stokes' Law, then using a calculated Mie scattering curve for the scattering angle to determine the distribution of particle sizes.

A summer student is currently just beginning to set up and test a vibration orifice aerosol generator based upon the Berglund-Liu design. The generator is claimed to be capable of producing monodispersed particles of liquid or solid materials if operated under carefully controlled conditions. Scientists at the Environmental Protection Agency and other laboratories have experienced difficulties in obtaining the desired size and reproducibility claimed by the designers. The laser Doppler spectrometer will be used to investigate the operating parameters of the vibrating orifice and to assign accuracy limits to its performance. Once calibrated, the particle generator will be used in conjunction with the light scattering instrument to carry out particle reaction studies.

An evaluation of the potential of coherent anti-Stokes Raman spectroscopy (CARS) for the use as a general analytical tool, for particulate analysis, and for gas analysis was undertaken at Molectron Corporation in Sunnyvale, California. Since that trip, one paper has been written.[1].

In the last year, the particle doppler shift spectrometer (PDSS) has been assembled and successfully tested. Preliminary studies have been made with the Berglund-Liu vibrating orifice aerosol generator (VOAG) as a particle source.

The PDSS is capable of resolving 0.1 μm size increments with similar accuracy in the 10 μm radius size range. In the form described previously, in the FY 1975 report, the PDSS was used to check the performance of a Royco model 225/508 and a Particle Measurement Systems ASSP. Both of the latter instruments were within their specifications, but neither showed the resolution or detail in the size distribution, nor had any means of internal accuracy check which the PDSS has.

The limitations on the PDSS at present are the following:

1) poor reliability of the EMR computer system for data storage and processing.

2) considerably less resolution available than is theoretically possible (this is due to the 100 channel capacity of the correlator and the slow transfer rate of data to the computer).

3) Convection currents in the scattering volume.

A new particle handling system to introduce particles into the scattering volume has been designed (in large part by David Bright). This system with a long vertical column with postions to control flow at top and bottom is being tested now. This system is meant to replace the wind tunnel arrangement.

We are also considering a fast Fourier transform instrument with 400 channels and frequency range translation as a replacement for the 100 point correlation. The FFT instrument would allow greater resolution and accuracy, faster data collection, and less dependence upon the state of health of the EMR computer.

A paper on the preliminary design and testing of the PDSS is being prepared for submission to Environmental Science and Technology. Included in the paper will be comments on the vibrating orifice generator. The data, even in preliminary form, show that the aerosol produced has considerably more "structure" in its size distribution than has been detected or assumed previously.

The three week trip to Molectron Corporation in spring of 1975 has resulted in the paper cited in the previous report, a second paper to be published shortly in Proc. Natl'l Acad. Sci. (US), and the establishment of a facility at NBS for study of non-linear optical spectroscopy. One aspect which will be considered is any application of techniques (other than CARS itself) such as inverse Raman, to particulate samples, and to gaseous samples.

References

[1]. Klauminzer, Gary,Hudson, Bruce and Chabay, Ilan, Coherent Anti-Stokes Raman Spectroscopy(CARS): Improved Experimental Design and Observation of New Higher Order Processes. *Submitted to Applied Physics Letters.*

33. Development of Sulfur Particle Analyzer

Project Leader:	R. L. McKenzie, Analytical Chemistry Division
Other Personnel:	D. B. Kittelson, M. Vermeersch, K. Kwok, D. Y. H. Pui, B. Y. H. Liu, K. T. Whitby, University of Minnesota, and Y. Kousaka, University of Osaka

Objective

The design goal of this project was to measure, in real time under field conditions, particulate sulfur levels ranging from ambient levels (about 1 microgram per cubic meter sulfate) up to source emission levels which may range up to as high as 50 micrograms per cubic meter.

Approach

The present configuration of the system which has been developed is shown in the schematic diagram in Figure 33.1, which indicates the principle that is being used. Aerosol samples enter the system through an electrostatic precipitator chopper which is turned on and off by a high voltage square wave. When the precipitator is on, it charges and precipitates the particles, removing them from the sample stream. When the precipitator is off, the particles flow through the precipitator into the flame photometric detector. This results in modulation of the aerosol concentration entering the flame photometric detector, which in turn results in a modulated output from the flame photometric detector. The modulated portion of the signal is proportional to the aerosol concentration in the sample. The flame photometric detector output is measured with the lock-in amplifier, which selectively amplifies the modulated or a.c. component of the signal, which has the frequency of the square wave high-voltage source on the chopper. Because the chopper does not modulate any gas phase materials, the system should not respond to gas phase sulfur species, for example, SO_2.

In the last Progress Report, work was reported that we did with a Meloy Model 180 flame photometric detector. A high sensitivity instrument, the Model SA-285, has been obtained and preliminary calibrations with sulfuric acid, using this detector have been made. Just two weeks after that instrument was received it was taken to Los Angeles for a two-week field study.

Progress

Figure 33.2 shows the calibration curve obtained for sulfuric acid using the Meloy 285 as a detector. Three calibration curves have been obtained, one with 0 ppb SO_2 as a background gas phase constituent, and two curves with, respectively, 30 ppb and 60 ppb SO_2. These calibration curves, shown in Figure33.2indicate that there is an SO_2 interference: the calibration curve is a function of the level of SO_2 in the sample. Some calculations have just been completed to characterize response of the whole system, which indicates that this type of behavior would occur if there is an error in setting the off-set voltage for the system, or in setting the span. An error analysis is now being done to see how great an error is caused by small misadjustments. In any case, the SO_2 interference is not a major problem, because the SO_2 can be removed from the sample by simply putting a scrubber in the sample line before the inlet.

The instrument as described above gives only a measure of the total sulfur in particles, and gives no information about the chemical form of the sulfur.

The second objective of this study was to be able to perform some speciation of the sulfur in the particles.

The first technique to be described is a thermal speciation system which can be coupled directly to the inlet of the particulate sulfur monitor just described. When the volatilization temperature of an aerosol that contains volatile compounds is reached for a particular compound, that particle will evaporate. Much of the vapor will be lost to the walls by diffusion. If the sample is subsequently cooled, the remaining vapors will recondense and reform particles, but these particles will be lost to surfaces in the system as they reform due to the high diffusional mobility of these small particles.

Figure 33.3 shows thermograms obtained for sulfuric acid, ammonium sulfate, and ammonium bisulfate. These thermograms were obtained by passing the aerosol through a heater and a condensor section, and then to a detector. The loss of particles is as one would anticipate for the volatilization properties of the compounds in these particles. Sulfuric acid aerosol losses begin to occur at about 30°C, and are essentially complete by 100°C. The 50% temperature transition for this particular material is 71°C. The ammonium salts of sulfuric acid do not begin to be lost from the sample until about 100°C, and the loss is essentially complete at 200°C. The midpoint of this transition is about 142°C. For these two particular cases, it is possible to distinguish clearly between sulfuric acid and its ammonium salts by this technique.

Two other temperatures that help to characterize this system are the ambient temperature, where all of the material is still present, and 200°C, where all of the material has essentially been lost from the sample. Any material left in the sample at 200°C would be what we will term refractory sulfur compounds. One disadvantage in making thermograms as just described in the field is that it requires long equilibration times to reach the various temperatures, and there are also many transient values introduced between equilibrium values. One has been able to take advantage of the four characterizing temperatures indicated above to eliminate these transients and to operate under continuous equilibrium temperature conditions.

Figure 33.4 is a schematic diagram of the thermal speciation system. The sample is drawn in simultaneously through four identical pathways which are respectively at ambient temperature, 71°C, 142°C, and 190°C. The second half of this system just provides a means of selecting the sample from a particular heater condenser pathway while simultaneously maintaining constant equal flows through all four pathways.

Figure 33.5 is a strip chart recorder made during the Los Angeles Freeway Study several weeks ago. The signal changes as one switches from one thermal pathway to another. The response time of the whole system is indicated on this curve to be about 1 minute. When the signals are converted from millivolt readings to sulfur concentrations, one finds the following values:

Temperature	$\mu gm/S/m^3$	% of Total Signal
ambient	.75 - .80	(100)
71°C	.70 - .75	10
142°C	.55	20
190°C	.50	70

This data indicates that the sensitivity of our system is about .1 μg of sulfur/m^3.

The above sample was taken on the upwind side of the San Diego Freeway when the wind was coming in off the ocean. The data indicates that only 10% of this sample was lost in the region where sulfuric acid would be lost, 20% of the sample was lost in the region where ammonium sulfate and bisulfate materials are lost, and 70% of the sample is in the refractory sulfur compound region. Part of the signal in the 190°C thermal pathway may be due to potassium or sodium metals, which have been shown earlier to cause a positive interference. (These salts would be expected to be in the refractory fraction of the sample.) However, the levels that would be required of these two metal ions, based on earlier studies, indicate that they would contribute only a minor part of the signal that is being seen in this sample region.

The second speciation technique that is being developed is termed an aerosol mobility chromatograph. The system, which is shown schematically in Figure 33.6, detects the change in the size of the aerosol upon exposure to different relative humidity conditions by use of a high resolution differential mobility analyzer. The sample is introduced and passed through a diffusion dryer and then through a Krypton 85 neutralizer which dries the sample and gives it an equilibrium Boltzmann charge. The sample goes through a differential mobility analyzer which selects a monodisperse fraction of that sample to be used for the rest of the evaluation. The monodisperse sample is equilibrated to new humidity conditions in the humidifier section, and the sample is subsequently analyzed with the second differential mobility analyzer. If the material contains hydroscopic species, the water content, and thus the particle size of the aerosol, will change under the new humidity conditions. This change may be detected in the second differential mobility analyzer. Calculations have been made based on the equilibrium vapor pressure data for sulfuric acid, and using Kelvin's equation to predict theoretically the change in water content of sulfuric acid droplets under varying humidity conditions. These calculations are shown in Figure 33.7 as the solid lines. One sees that as the relative humidity goes up, the particle diameter increases. The data points are for sulfuric acid aerosols measured in the aerosol mobility chromatograph. The agreement between theory and the experiment is very, very good.

Figure 33.8 provides a demonstration of an actual separation of two different sulfur species. Potassium sulfate and sulfuric acid aerosols were generated and mixed, and then fed into the system. The solid curve shows that with no humidification between the first and second aerosol mobility analyzers, both materials come out together in the same peak. However, when the relative humidity is raised to 53%, separation occurs. Under these conditions, sulfuric acid aerosol will grow as it picks up water; potassium sulfate, however, will not grow, as 53% relative humidity is still below the deliquescent point for potassium sulfate. The different responses of the aerosols to the change in relative humidity results in different aerosol equilibrium sizes, and consequently, in different electrical mobilities. This provides the basis for the separation that is shown in Figure 33.8.

Conclusion

In summary, one now has a prototype system that meets the design objectives for the project, and begins to think in terms of possible production configurations for the system. Future work includes the following items:

- Evaluation of the SO_2 interference.
- Complete calibration curves for sulfuric acid and for sulfate salts.
- Evaluation of the system with respect to metal ion interferences.
- Evaluation of burner block configuration.

  The response time of the slowest component in this system will determine the maximum chopping rate. The maximum chopping rate in turn determines the overall response time of the instrument. Calculations of the time scale of the events that occur in the flame indicate that these processes should all occur within tenths of a second or less. However, data indicates for the burner block in the Meloy, that events occur that take as long as several seconds. This is due to absorption-desorption from the walls and other surfaces in the burner block. A burner block to minimize this, and decrease the response time of the system is being designed.
- Characterization of the aerosol mobility chromatograph with respect to ammonium salts of sulfuric acid, and also with respect to other compounds such as nitrates which may possibly act as interferences in this particular application.

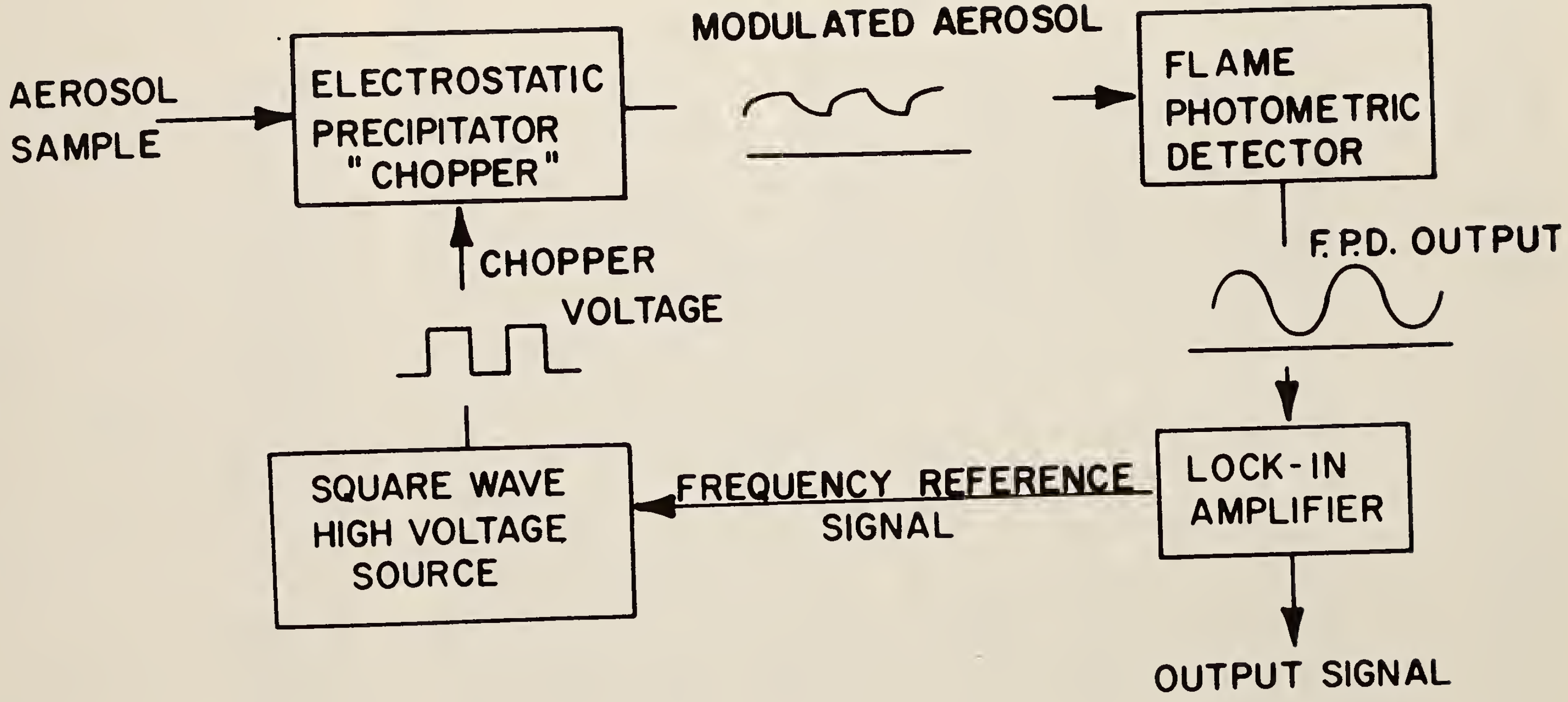


Figure 33.1 Pulsed Electrostatic Precipitator Total Particulate Sulfur Monitor

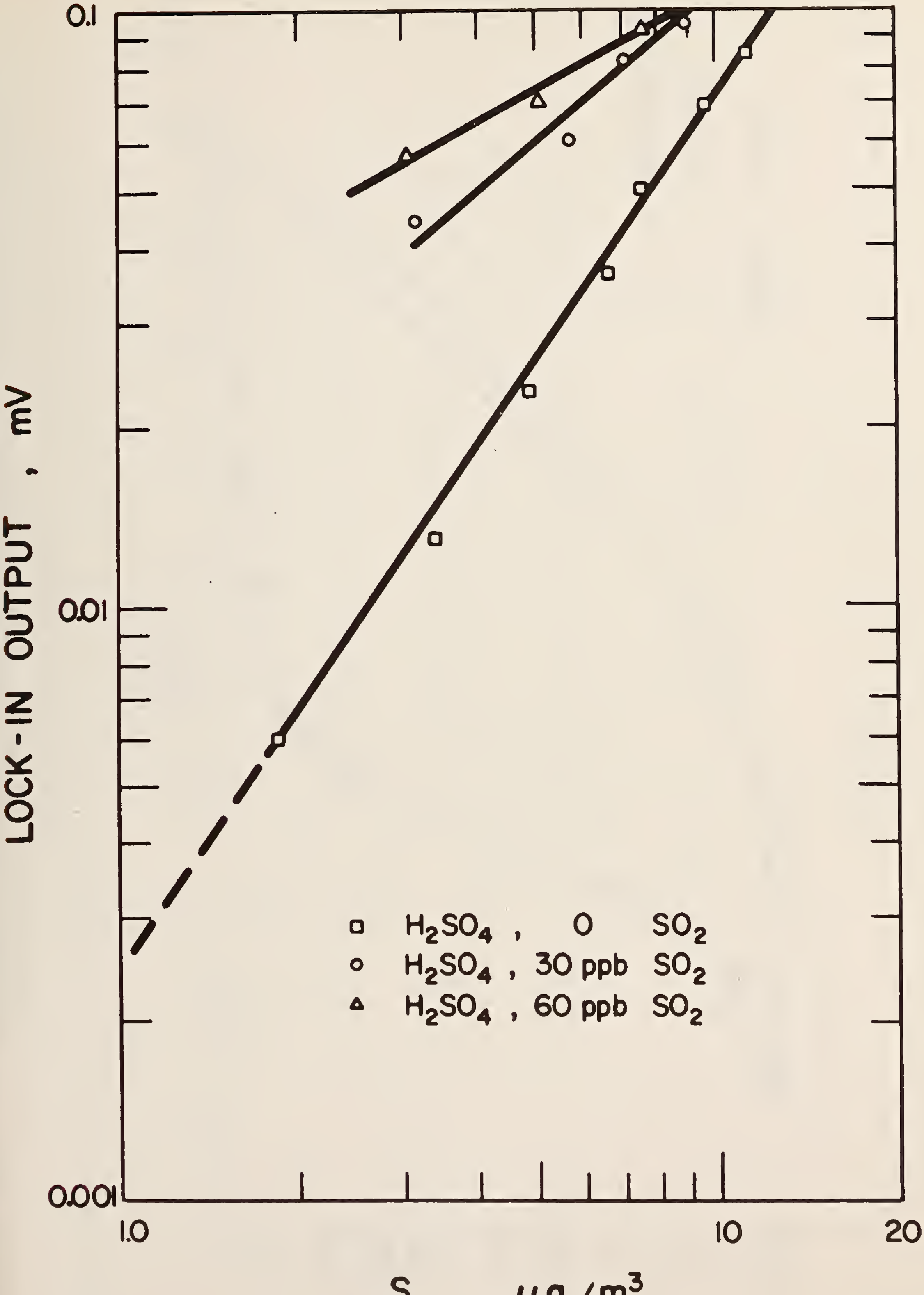


Figure 33.2 Calibration curve obtained for Sulfuric Acid using the Meloy 285 as a detector.

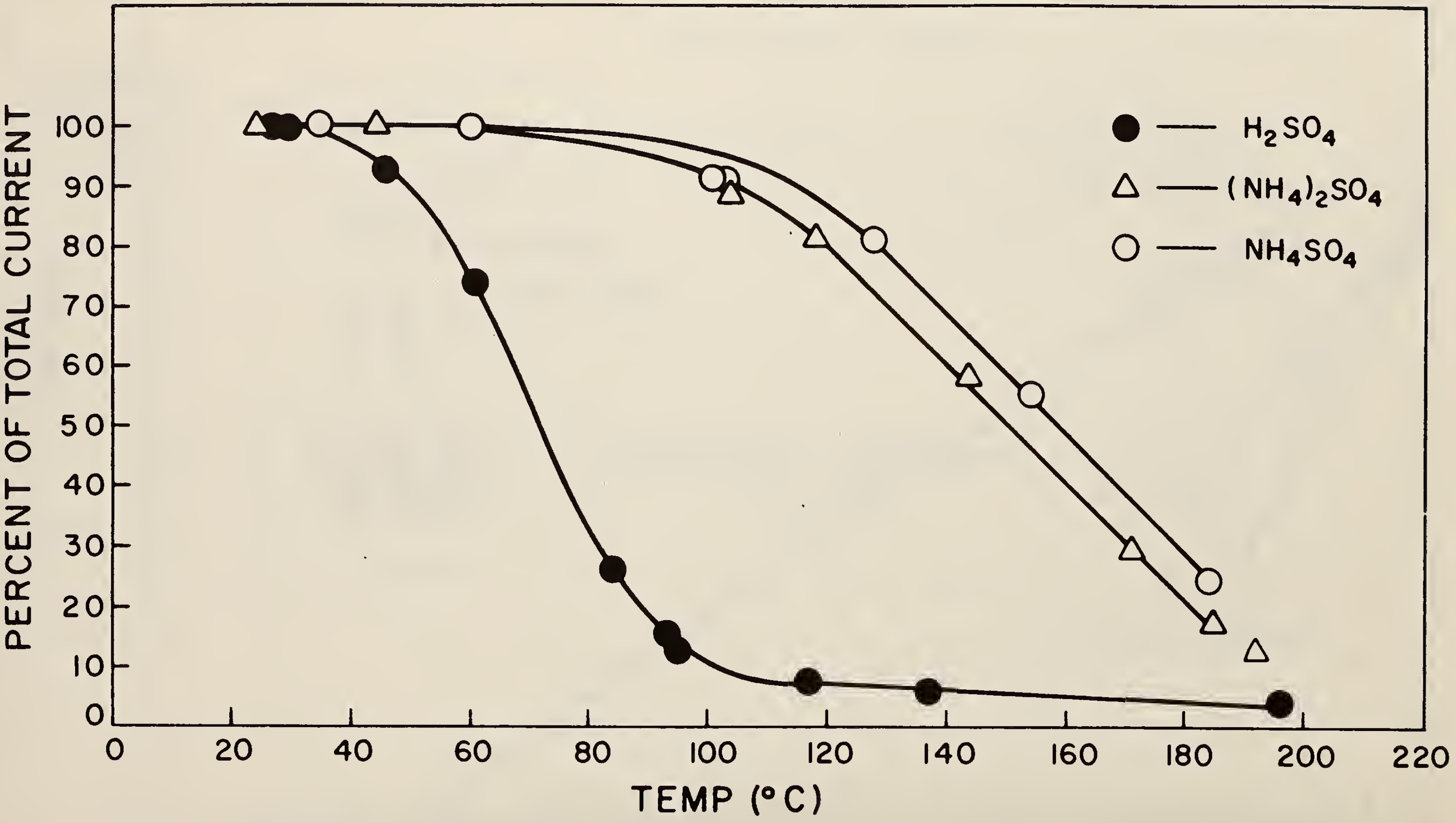


Figure 33.3 Thermogram of various Sulfates in CH_4.

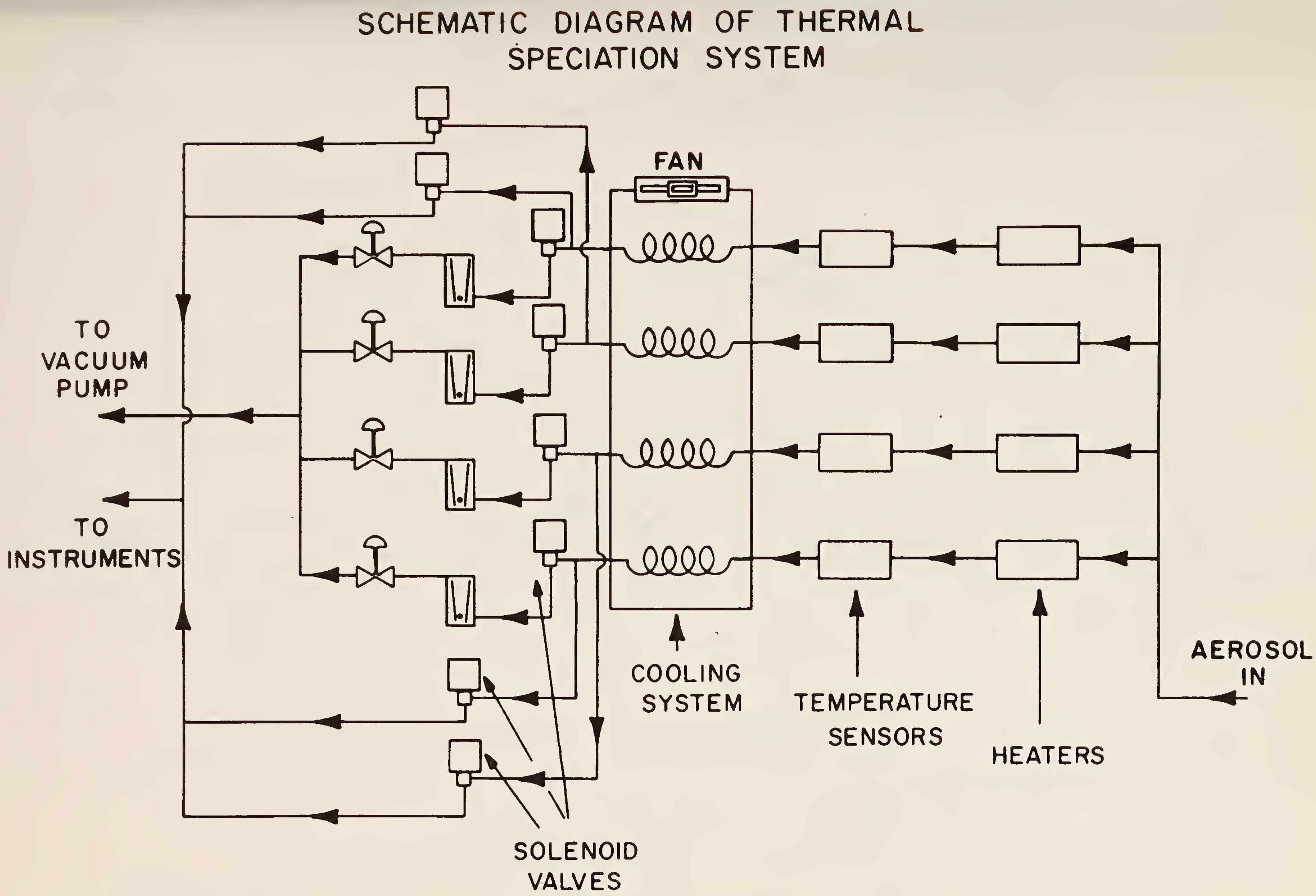


Figure 33.4 Schematic Diagram of Thermal Speciation System.

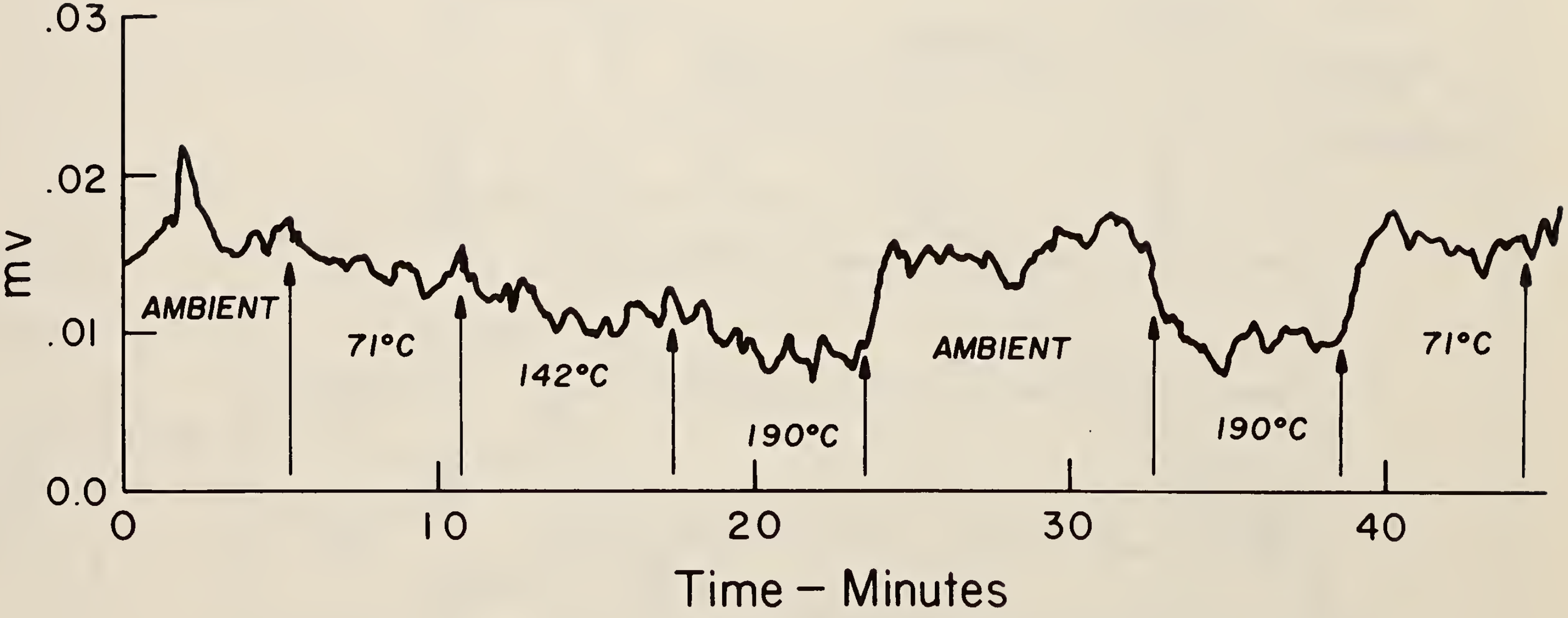


Figure 33.5 Strip chart record of Los Angeles Freeway Study.

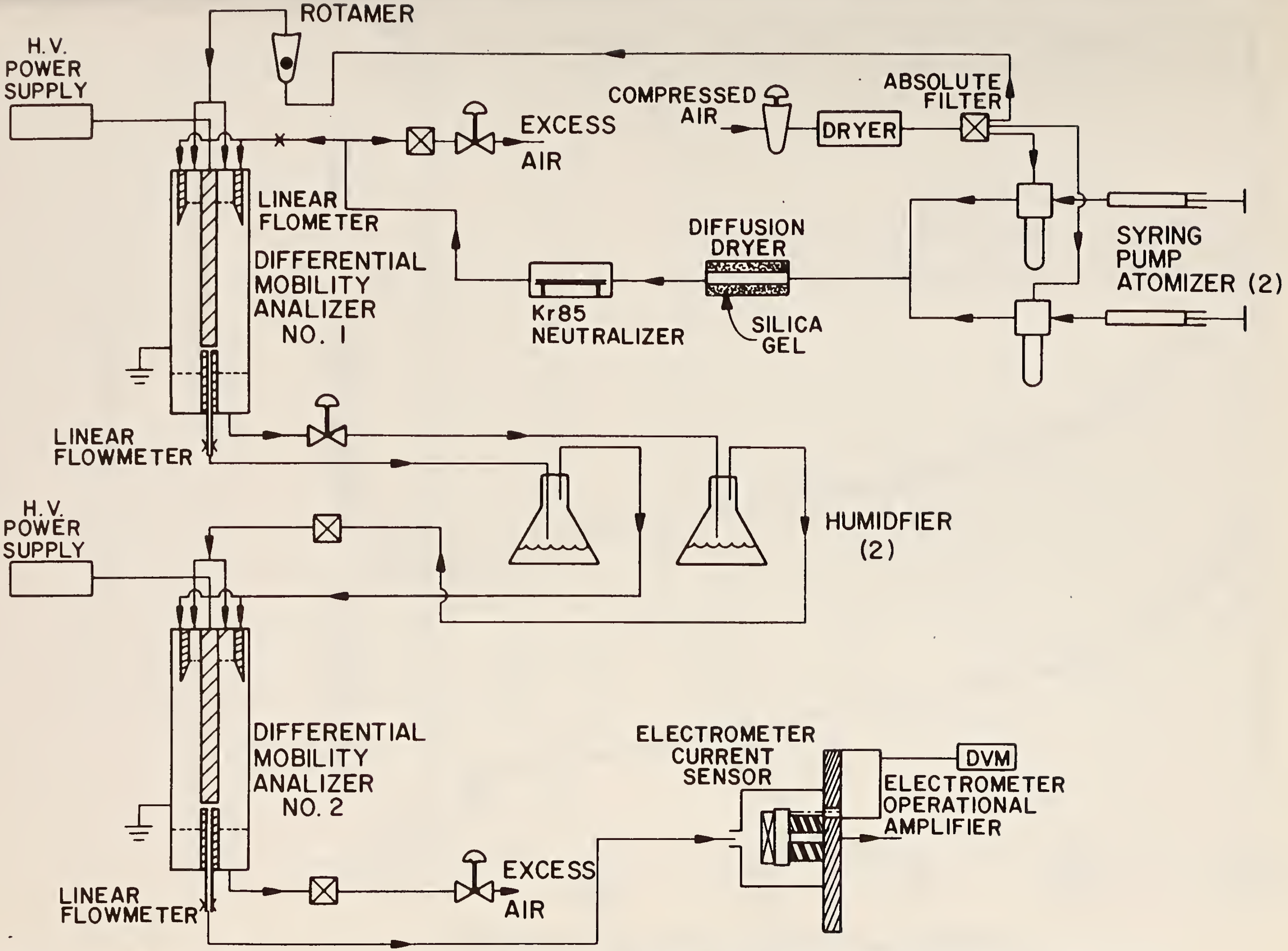


Figure 33.6 Schematic of aerosol mobility chromatograph speciation technique.

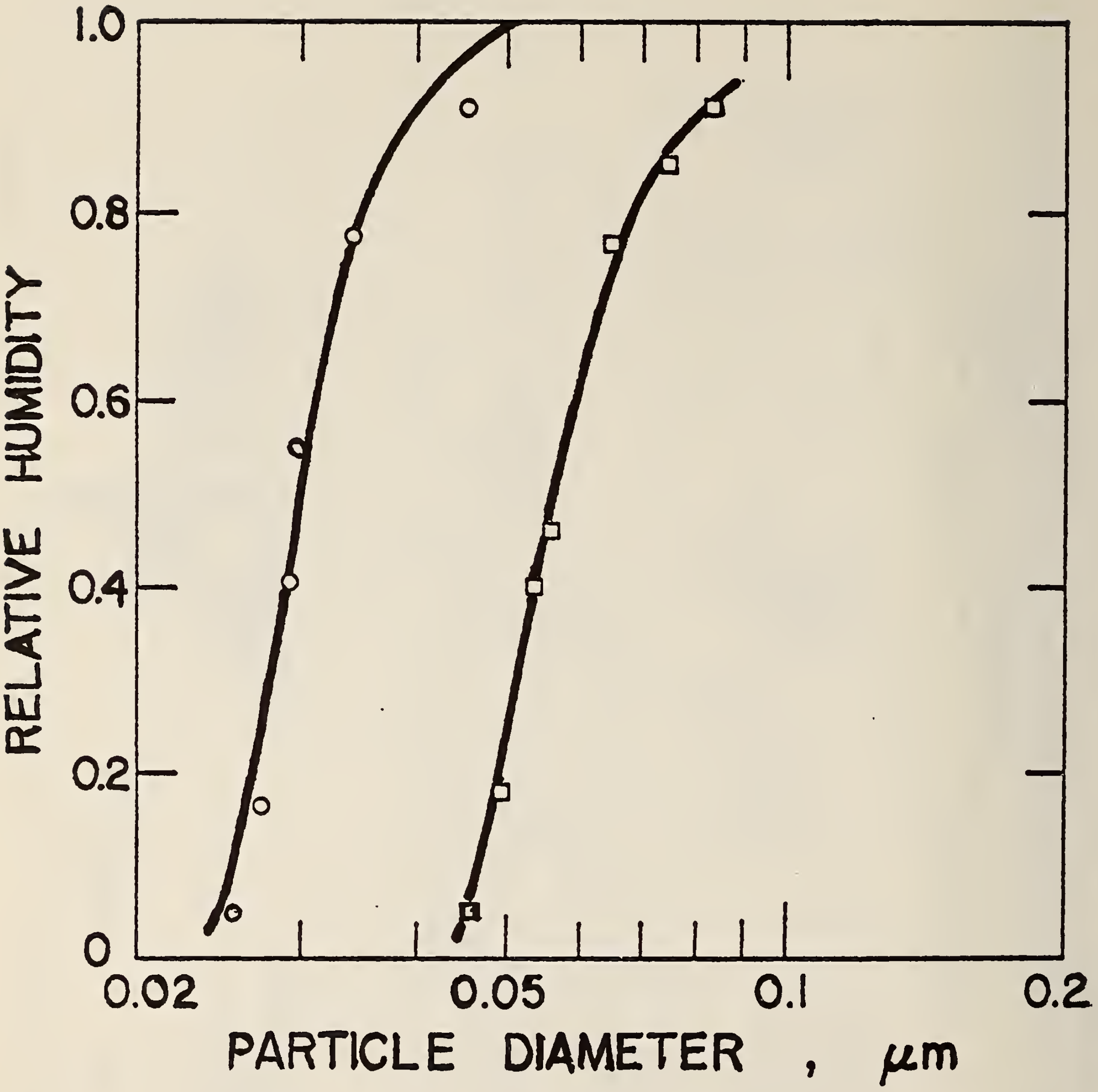


Figure 33.7 Equilibrium Vapor Pressure Data for Sulfuric Acid.

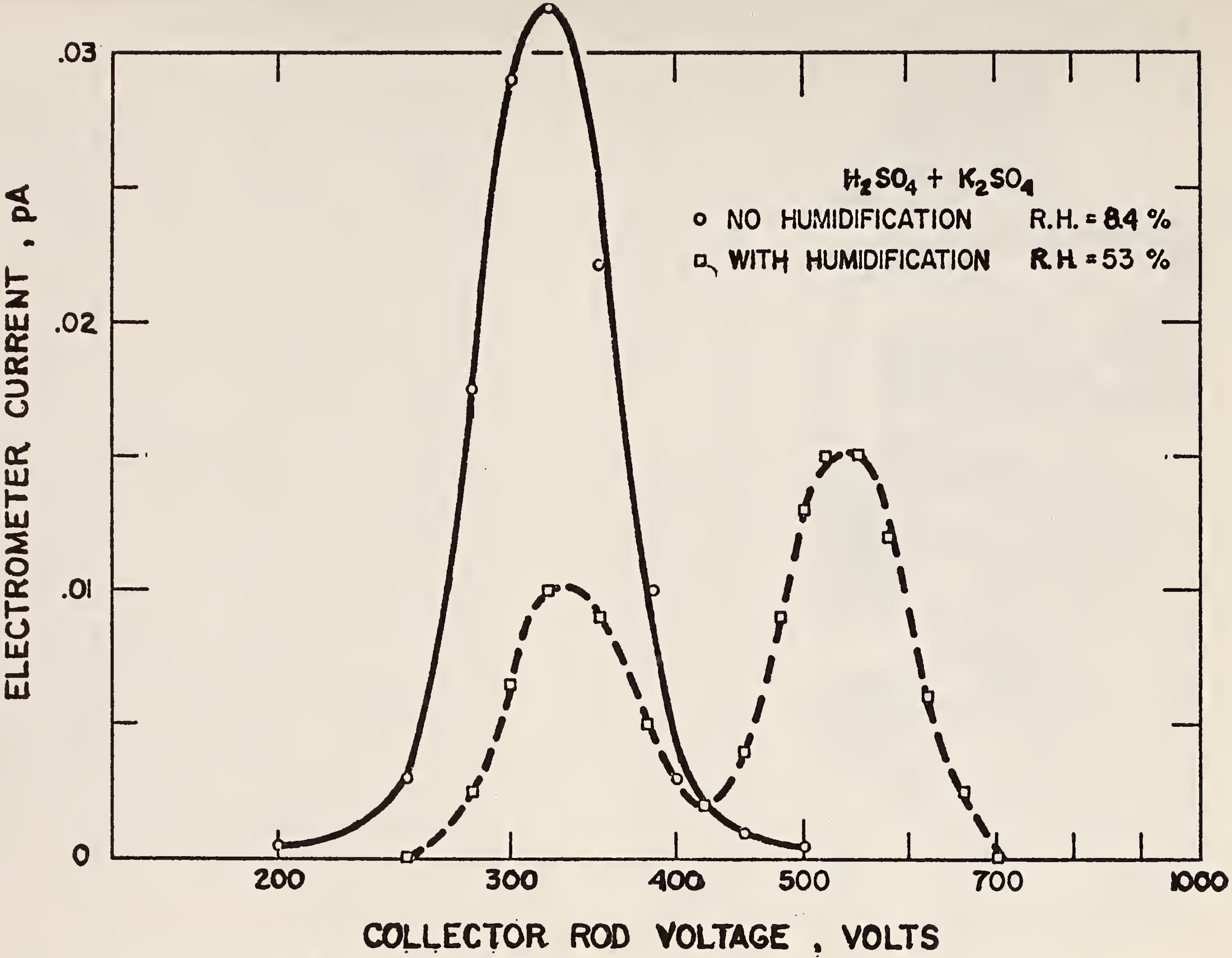
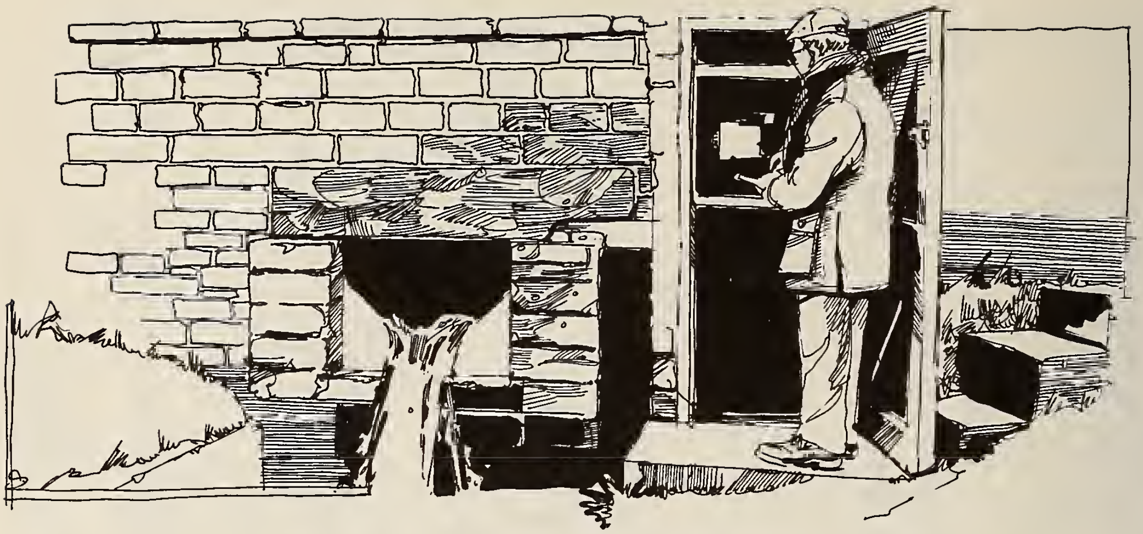


Figure 33.8 Separation of Potassium Sulfate and Sulfuric Acid Aerosols.



34. Flow Measurements for Water Pollution Abatement

Project Leader: G. Kulin, Mechanics Division
Other Personnel: R. W. Davis, K. E. Lofquist (part-time),
A. L. Lembeck, T. Robusto, Jr.

Objective

The objectives of the project are (1) to improve the measurement of water velocities as practiced in the field, with emphasis on low velocities (less than 1 ft/s) and on the use of current meters for velocity sampling in open channels; and (2) to improve field measurements of the volumetric flowrate of water and wastewater. There is a strong connection between the two objectives in that the velocity-area traverse is one of the most basic and frequently used methods for determining flowrate and for field calibrating flowrate measuring instruments. Attainment of these objectives is motivated by needs for: better measurement of the very low velocities which play major roles in lake and estuary dynamics and which have become increasingly important in view of the intense interest in water quality control and marine disposal of thermal discharges and other wastes; the establishment of guidelines for accurate and consistent wastewater-discharge compliance and enforcement monitoring, and for other flow measurements needed to satisfy regulatory requirements; and promulgation of such guidelines among users by publications, workshops, conferences, short courses, etc.

Approach

The approach emphasizes analytical, computational and experimental flow measurement investigations in-house, complemented by the maintenance of extensive contacts with users who actually make flow measurements in the field. The purpose of the field contacts is to observe flow measurement problems and error sources as they occur in the field in order to continuously assess measurement needs versus existing capability and to provide meaningful input for the laboratory program. The field contact work also fosters the transfer of measurement capability and information from NBS to field users.

The laboratory program includes: experimental studies of water velocity and flowrate measuring devices and methods to determine performance limits and error sources; development of analytical and computational models to support, complement and extend this experimental work; and application of these results to provide guidelines and recommended practices for flow measurements. The future high performance water tunnel and the almost completed open channel will be the major laboratory facilities for the velocity and open channel flow measurement efforts respectively.

Progress

Flow measurement guidebook. "A Guide to Methods and Standards for the Measurement of Water Flow," G. Kulin and P. R. Compton, was published in May, 1975 as NBS Special Publication 421 and is available for purchase from the G.P.O. ($1.65, Cat. No. C13.10:421). It has also been distributed directly to appropriate EPA personnel and to selected users whose measurement problems were discussed as part of the field contacts effort of the project. The total distribution to date has been approximately 1,000 copies, with about half of that number accounted for by G.P.O. sales or direct requests to NBS.

The guidebook was prepared for the following purposes:

1. To collect in one document and briefly describe the best sources of information on good flow measurement practices. Although several good flow measurement manuals have been available, in our opinion no single publication existed which directed field users to all of the information needed for good measurements. Accessibility of these sources was emphasized.

2. To caution users concerning error sources and pitfalls in the use of instruments and procedures. These errors were quantified wherever possible using our own experience and information gathered from available literature. Our field contacts had indicated that one of the shortcomings in other flow measurement publications (in the eyes of the users) was their failure to indicate the errors introduced by departures from "standard" practice.

Additions and comments from readers will be incorporated in a projected future revision of this guidebook.

Ad hoc committee on wastewater flow measurement. The Environmental Protection Agency has an immediate need to establish flow measurement guidelines for the large number of industries and municipalities which are being issued effluent permits. Because these permits are issued in terms of a total daily pollutant loading, all dischargers must monitor the flowrate as well as the pollutant concentrations of their effluents. Legally and technically acceptable criteria for self-monitoring flow measurements (by industries) and for calibration checks (by regulatory agencies) must be established. EPA requested the Mechanics Division to organize an ad hoc group of Federal flow measurement experts to address this problem, and a meeting of this interagency panel was held at NBS on June 24, 1974. The foregoing flow measurement guidebook responded to many of the issues raised during that meeting, and future activities by this panel depend in part on response and follow-up to that initial guidebook effort.

Open channel flow measurement-flumes. The Parshall flume is probably the most widely used flow measuring flume. It is an empirical device which resists purely theoretical analysis. Experiments were made in the NBS hydraulic laboratory on a three-inch Parshall flume to determine flowrate errors caused by bottom slopes (the flume should be level) and by incorrect sidewall convergence angles. These two error sources stem from common installation and fabrication errors, and no guidelines exist for adjusting the published flow tables for these effects. The experiments were supported and guided by prior error estimates which had been made using semi-analytical approaches based on reasonable assumptions. This analytical work also provided a rational basis for extrapolating the experimental results to larger flumes. The results indicated, for example, that for flume bottom slopes of one-half percent and more, errors of more than 10 percent can be introduced by using uncorrected published data for the lowest flowrates.[1]

The Palmer-Bowlus flume is another popular type of wastewater flow meter and a discussion by G.Kulin [2] calls users' attention to possible errors of up to 8 percent at the low and high extremes of flow if certain precautions are not observed.

Open channel flow measurement--computer models. The work on the applicability of computer simulation models to solutions of flows over certain types of flumes (two-dimensional Palmer-Bowlus) or broad-crested weirs resulted in a paper.[3]. In this study, the operational range of the two-dimensional flume was extended to head-length ratios for which the one-dimensional theory(the only previously available analytical approach)lost its validity. Effects of changes in flume bottom geometry, channel slope and upstream velocity profile were investigated numerically. Experimental verifications were obtained in a laboratory flume of six-inch width and crest length. The results also will provide guidance for the effective conduct of the flume performance experiments in the new open channel which is described in the following section.

Open channel. Construction of an open channel facility will be completed in August 1976. This open channel is necessary for (1) evaluations of upstream effects on flowrate measuring flumes, veirs and other devices, (2) development of guidelines for traversing small conduits and sewers with current meters and ultrasonic flowmeters, (3) determination of the hydraulics of flow in partly full pipes, i.e., sewers, this information being needed for improvements in certain methods of sewage flow measurement, and (4) investigations of the feasibility of using laser-based devices for flowrate determinations in sewers and other open channels.

The open channel is an open circuit system employing the existing reservoir and pumping system of the laboratory. It also uses the constant-head inlet tank which is part of an existing gravity-flow water tunnel. The basic working section is 40 feet long and is a 3 x 1-1/2 ft. rectangle in section. This section can be replaced in the future with a circular section for sewer-related flow investigations. The channel slope is adjustable and the flow capacity is 10 cubic ft. per second. The basic flowrate measurement is a rectangular weir in the outlet tank, which will be calibrated in place.

Flow in rectangular open channels. There is surprisingly little published information on the detailed characteristics, specifically velocity distributions, of open channel flow in artificial conduits of various shapes and roughness. Some of these gaps will be filled by the work to be done in the NBS open channel. However, enough information has been gleaned from the literature to permit at least the determination of the useful limits of the one-point (six-tenths depth) method of velocity traversing in rectangular conduits of appreciable depth-width ratio. Because this is considered worthwhile information for the user community, a technical note on the subject is being prepared without awaiting future NBS work on guidelines for traversing small conduits.

Current meters. The experimental investigation of the low velocity performance of Price and Pygmy current meters in a small towing tank has been completed. The velocity range was generally from 0.1 ft/s to 0.5 ft/s, although in some cases the Price meter was used at velocities as low as 0.06 feet per second. This work includes: investigation of the repeatibility of meter performance at low velocities; experiments on the effect of internal friction (as grossly evidenced by spin tests) on the threshold velocity and low velocity behavior of Price meters; sidewall and bottom proximity effects on bucket-type current meters; effect of a small angle of tilt on Price meters at low velocities; and estimates of the errors involved in extrapolating routine calibration curves (with velocities to 0.25 ft/s) to 0.1 feet per second.

Additionally, an analytical model of bucket-wheel, vertical-axis current meters was developed which permits evaluation of the errors introduced by lateral velocity gradients in the flow. Errors caused by the presence of the observer's body in the stream during rod-supported "wading" measurements were evaluated theoretically. The results suggest that the presently recommended wading position can introduce significant systematic error, but field data on this subject are meager.

Also evaluated theoretically were the effects on meter rotation of the proximity of the torpedo-shaped weights used during cable suspension of current meters. These results were compared with prior data obtained in the large towing basin on the old NBS grounds.

All of the foregoing results are now being prepared for publication.

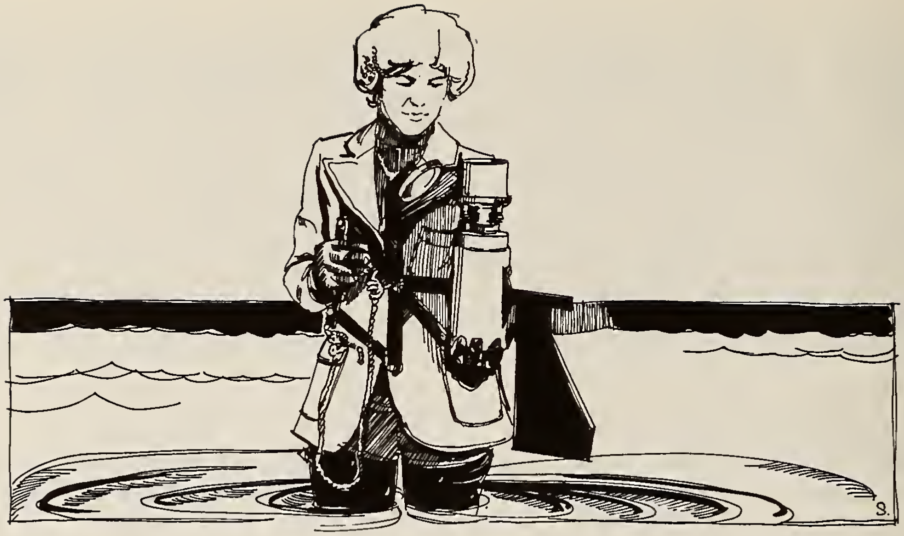
Water tunnel. Completion of the high performance, 24-inch test section water tunnel has been hampered by continual delays owing mainly to the contractor's difficulties with certain subcontracts. Contract monitoring and other activities in support of the tunnel contract continued throughout the reporting period. The earliest commitments of the completed water tunnel to the water pollution flow measurements program will be for establishment of high quality, low velocity reference flows in the test section and for the evaluation of turbulence effects on vertical-axis current meters.

Flow measurement conferences. A three-day conference on Flow Measurements as related to National Needs was arranged and hosted by NBS on February 26-28, 1974, to provide a forum at which regulatory authorities, instrument users and manufacturers could address problems of flow measurements in the field. One day of this conference was devoted to water and wastewater flow measurements, and the program arranged for that day was a direct follow-up of the field contacts activity which had preceded it.

A follow-up symposium on Errors in Open Channel and Closed Conduit Flow Measurement: Their Sources, Assessment and Resolution is now being planned for February 23-24, 1977 at NBS. This meeting proposes to provide a forum for identifying additional error sources in flow measurement, formulating error analysis techniques and recommending techniques for resolving uncertainties. Additionally, it will provide the stimulus for cooperative industry-government activities for reducing uncertainites in all phases of open channel and closed conduit flow measurement. Approximately one half of the sessions will be devoted to open channel flows of water and wastewater.

References

[1]. Kulin, G. and Davis, R.W., Effect on Parshall Flumes of Slope and Geometry Changes, in press.
[2]. Ludwig, R.G. and Parkhurst, J.D., Simplified Application of Palmer-Bowlus Flow Meters, discussion by G. Kulin, *Journal of the Water Pollution Control Federation*, 48, January 1976.
[3]. Davis, R.W., Numerical Modeling of Two-Dimensional Flumes, *submitted to the Journal of the Hydraulics Division, American Society of Civil Engineers.*



35. Water Sampling and Sample Handling for Trace Element Analysis

Project Leaders: D. A. Becker, S. H. Harrison, Analytical Chemistry Division

Objective

The validity of trace element measurements is directly related to the validity of the sampling procedures used. This project aims to study and develop water sampling and preanalysis handling procedures for trace element profile determinations. The objective of this work was separated into four phases: (1) development of the analytical technique, (2) development of a water sampler, (3) use and evaluation of the water sampler, and (4) applications to environmental problems.

Approach

In order to investigate sampling protocols, an analysis technique capable of multielement determinations on a single sample was needed. Non-destructive neutron activation analysis of freeze dried water was chosen for this purpose. This technique was used to evaluate a Teflon water sampler developed in our Division. This evaluation consists of replicate sampling studies and a comparison of results with those from a popular commercial water sampler. To demonstrate that the sampling, treatment and analysis procedure developed is applicable to environmental problems, a study of two waterways, suspected of abnormal trace element content, was initiated.

During this evaluation, the sampling, storage and handling techniques used are reevaluated, and changed if necessary in order to provide a convenient, workable and scientifically valid water sampling protocal.

Progress

Radioactive tracer studies for determining the trace element retention of 21 elements during the freeze drying process have been completed. The results show that all but the most volatile elements (Hg, I, and perhaps Au) are quantitatively retained in a residue resulting from the freeze drying of 100 g of filtered river water.

After establishing a technique for preconcentration of water, the development and study of sampling techniques was initiated. A Teflon water sampler, which was designed and constructed at NBS is under evaluation. To date, most of the evaluation has consisted of determining the sampling error for different kinds of water systems. The method chosen was replicate sampling of a location over a moderately long time interval about two hours. Sampling error was defined as

$$SE = \sqrt{(SD)^2 - (AE)^2 - (FDL)^2}$$

where SD = the relative standard deviation of the determinations in the replicate samples, AE = the analytical error and FDL = the freeze dry loss. For suspended particulates the last term is not applicable.

The kinds of water systems investigated were a fresh water stream, a mixing zone in a river and a large estuary, at the mouth of its main tributary. The results for both the dissolved species (determined as freeze dried filtrate) and the suspended particulates are complete. As one might expect the fresh water stream is a well mixed system and the standard deviation of values for a single element in the replicate samples was generally determined to be less than 20% and for many elements, less than 10%. On the other hand, the estuarine locations are not as well mixed and the data show some indication that tidal changes cause dissolution of trace elements from the sediments into the aqueous phase.

Adopting a technique used by de Groot[1] and others, suspended particulate data were normalized to the element scandium. For the replicate sampling studies, normalizing suspended particulate values serves to smooth the data, particularly in the case of the estuarine samples.

Another part of the evaluation was to determine if the sampler construction materials would contaminate the water samples. This was assessed by running highly purified water through the sampler and filtering unit and then analyzing the water to determine if there was any increase in trace element content over the normal analytical blank. The results of this experiment appear in Table 35.1. (The polyethylene bag is the predominate analytical blank.) It can be seen from Table 35.1 that Na is the only element which is abnormally high in the "Sampling Blank" sample. Although the Co value of 21 nanograms is about twice as high as the largest value determined in the polyethylene bags, the range of Co values in these bags was so great that this value could be accounted for by inhomogeneity in the polyethylene.

To demonstrate the applicability of the described sampling and preconcentration scheme to aquatic environmental problems, a study of two estuarine systems was undertaken.

In cooperation with Robert Huggett of VIMS (who provided a boat and crew for sampling) a heavy metal characterization of Woods Creek was begun. Woods Creek is a small marshy waterway which flows into Skiffes Creek, and subsequently the James River near Fort Eustis, Virginia. A Dow Chemical plant dumps liquid effluent that is reportedly high in Zn into this creek. The problem is to determine the fate of the Zn in this waterway. Nine stations were sampled over a two-mile stretch of Woods Creek yielding filtered liquid, suspended particulates, and sediment (top cm) samples for each station. The liquid and suspended particulate samples have been analyzed for Zn and 10 to 20 other elements.

The normalization technique described above enhances the information obtained from the suspended particulates, that is, enrichments of elements relative to crystal material (as indicated by scandium) can be followed down the stream. Figure 35.1 shows the effect of normalization on two groups of elements. Completion of this project will require combining our data on filtered liquid and suspended particulates with sediment data from Mr. Huggett.

Phases 1 and 2 of the project (development of analytical technique and development of water sampler) are essentially complete. The primary objective of phase 1 was to determine if freeze drying (or lyophilization) of water was a viable technique for trace element preconcentration. The results of this work were published by S. H. Harrison, et al. in the August 1975 issue of Analytical Chemistry. Phase 2 involved the development of a Teflon water sampler with special features not presently available in commercial water samplers. The design and operating characteristics were described in a talk presented at the 7th Materials Research Symposium, October 1974, in Gaithersburg, Maryland. The manuscript of this talk appears in the Proceedings of the Symposium.

Phases 3 and 4 of the project (the use and evaluation of the water sampler and its application to sampling studies) are essentially complete. Because of the nature of phase 3, the sampler evaluation is an open ended project, but that part supported by the Office of Air and Water Measurement is complete.

For the most part, phase 3 consisted of replicate sampling studies (to determine natural variations of trace element concentrations at a single location) and data treatment studies. Much of this work is reported in the Proceedings of the 7th Materials Research Symposium referenced above, and some of it was presented at the 1975 Annual Meeting of the American Nuclear Society, June 9, New Orleans.

Changes and improvements in the techniques developed in all four phases are continuing, as experience dictates. An example of this is recent work on improving cleaning procedures of the polyethylene film used for making the water sample bags. Using a 24-hour washing period in 5 N HCl prior to the customary HNO_3 washing, the average Fe concentration in the film has been reduced by 50% (compared to the previously reported value in the Analytical Chemistry paper), the average Co concentration by an order of magnitude, and the average Mn concentration by almost an order of magnitude.

References

[1]. deGroot,A.J. and Allersma, E., Conference on Heavy Metals in the Aquatic Environment.,Nashville, Tenn. (December 1973).

TABLE 35.1

BLANK ANALYSIS DUE TO SAMPLING AND FILTERING PROCEDURE SAMPLING BLANK (118.57g PURIFIED WATER)

	Na	Br	Sc	Cr	Fe	Co	Zn	La
Total Nanograms in Sample	4400	66	0.21	440	1200	21	160	2.0
Range of Nonograms in Polyethylene Bags	230-2600	320-520	0.05-0.29	480-600	400-1900	0.36-11	60-330	1.2-2.7
Average Nanograms in Polyethylene Bags	1400	400	0.14	520	880	5.6	160	1.8
Nanograms in 118.57g of Purified Water[a]	7.1	ND	ND	2.4	5.9	ND	4.7	ND

[a] E. C. Kuehner, R. Alvarez, P. J. Paulsen, and T. J. Murphy, Analytical Chemistry, 44, 2050-2056 (1972).

ND = Not Determined

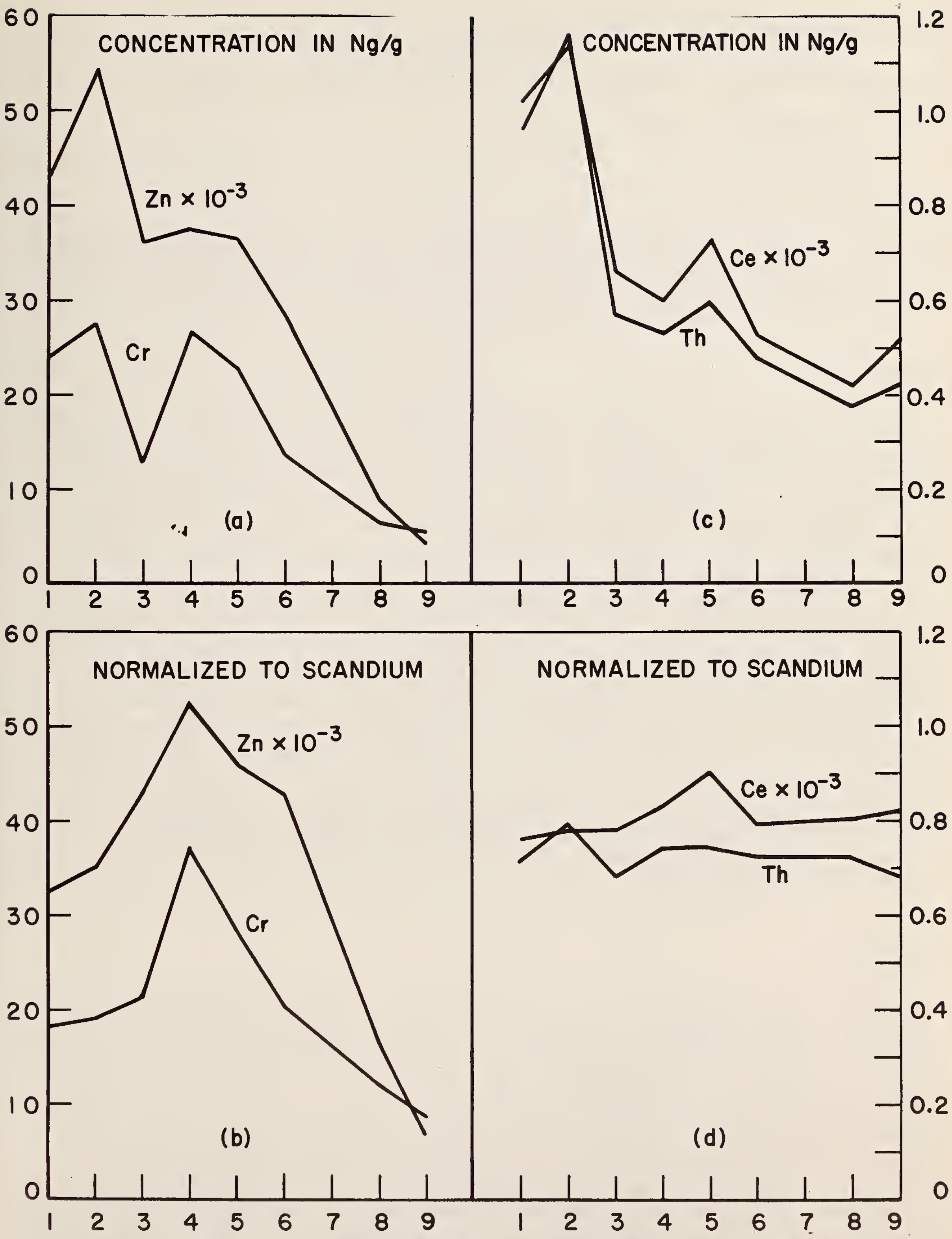


Figure 35.1 Plot of heavy metal concentrations and scandium normalized concentrations (x/Sc) of suspended particulates vs. sampling station in Woods Creek where station 1 is the headwaters of the creek and station 9 is just below the confluence of Woods and Skiffes Creeks. Distance between sampling locations is ∿equal.

36. Development of a Deep Sea Ocean Sampler

Project Leader: Meyer Waxman, Heat Division

Other Personnel: Harry Davis

Objective

Design, build, and test a deep-ocean biological water sampler, simple enough to be used by oceanographic researchers having access to only simple and unsophisticated vessels.

Approach

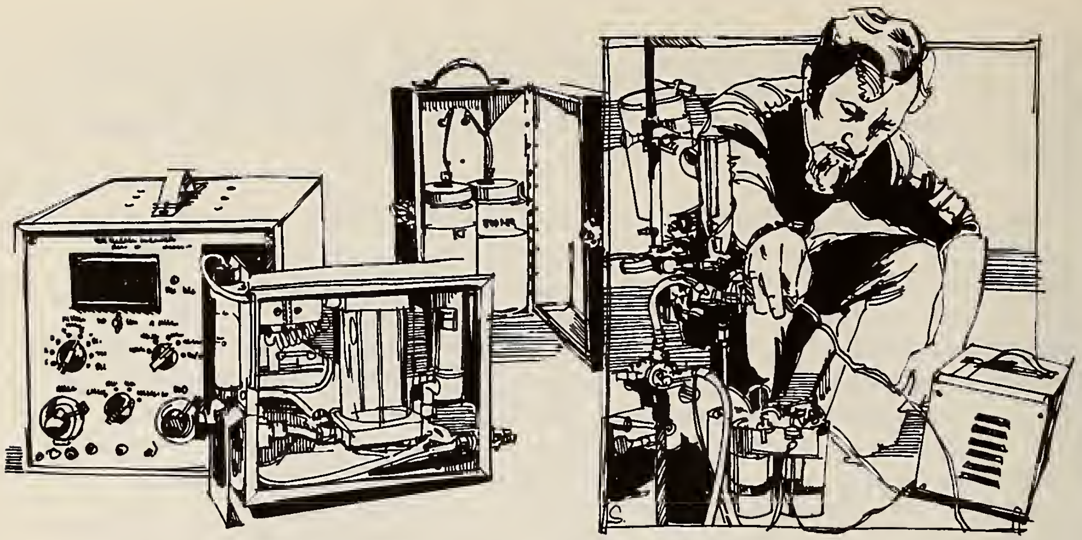
Initial design considerations included the utilization of the potential energy of the ocean with depth, of a free-falling piston within a cylinder and of an evacuated vessel to be opened at an appropriate time. The apparatus was to be a self-contained unit with provisions for a sequence of programmable events to take place on the ocean bottom. These were to include allowing time after bottom impact for adequate settlement of ocean-bottom sedimentation, allowing for equilibrium of the vessel's internal and external pressures, flushing of the vessel prior to its filling and releasing the sampler, after filling, for return to the ocean surface. All necessary energy for the operation of the different events were to be derived from compressed gas, batteries, or wound springs. We chose to select the latter concept because of its proven dependability in numerous technological applications. Industrial engineers, experts with both electro-mechanical and mechanical spring devices, strongly advised the sole use of the latter, again because of proven reliability.

Progress

A deep-ocean environmental sampler has been constructed to tolerate an internal pressure 15,000-20,000 psi with a marked safety factor. The sampler has been tested in a high pressure testing facility made available by the U. S. Navy. It is autoclavable and capable of maintaining sterility, as shown by studies carried out at the University of Maryland. The sampler permits recovery of samples without decompression. It can be used as an incubation chamber, with nutrients added to the sample and for the withdrawal of aliquots of the sample for analysis or transfer to other incubation units without depressurization of the sample. The sampler has been designed so that it is deployed closed, sterile and internally pressurized, and at the site of sample collection, opens, collects a sample, closes, and is retrieved with the samples maintained under in situ pressure.

A cruise was accomplished February 11-14, 1976, aboard the R. V. Eastward to the Puerto Rican trench. Two successful casts were obtained. The first successful cast was at a depth of 6,800 meters. The depth was calculated from reversing thermometers and from the internal pressure of the sampler upon retrieval and, in addition, readings made with a pinger. The water sample was subsampled using 4 (3 ml) syringes, filled by release of the in situ pressure (approximately 680 atmospheres. The syringes were immediately repressurized to 10,000 psi at 3°C. In addition, 2.5 ml subsamples were collected and added to MSWYE broth (9.0 ml). The nutrient broth was incubated at 3°C and good growth has been obtained. Cultures are presently being isolated. In addition to the successful retrieval of the first pressurized sample, the second cast provided a sample brought back under pressure from 3,430 m. On testing the internal pressure of the sampler on retrieval, the depth of the cast was confirmed and the reversing thermometer calculations also provided evidence of the cast at the depth indicated. We have maintained the water sample, under pressure, at approximately 343 atmospheres and have been able to introduce nutrient without decompression. These samples are still under pressure at 3°C. We anticipate being able to determine evidence of microbial growth and uptake since a radioactively labled substrate was introduced into the pressure chamber.

Work is progressing well on perfecting the sampler, that is, to provide transfer under pressure to fresh culture chambers and to improve the mechanism for introduction of nutrients under pressure. The sampling devices are also being improved to withstand repeated heavy duty use in the field.



37. An Electrochemical Chlorine Flux-Monitor

Project Leaders: G. Marinenko and J. Devoe, Analytical Chemistry Division

Other Personnel: D. Friend, J. L. Andrews, A. A. Bell, D. E. Braun, F. C. Ruegg, J. K. Taylor, R. Shideler and R. Huggett, Virginia Institute of Marine Science

Objective

The work described here deals with research leading to the development of an absolute, coulometrically calibrated chlorine flux-monitor capable of measuring chlorine in water down to 10 ppb.

Approach

Chlorine, chloramines, hypochlorite and other higher states of oxidation of chlorine will oxidize iodide to iodine at proper pH. Under select conditions one can separate some of the individual chlorine species and chloramines, taking advantage of different rates of oxidation of iodide. The initial effort, however, was directed at the determination of total residual chlorine. In the reaction with iodide one mole of chlorine produces one mole of iodine. Thus, monitoring the molar concentration of iodine is equivalent to monitoring the molar concentration of chlorine.

An electronic measurement package was designed and constructed to complement the electrochemical flux-monitor cell. Such an instrument fulfills the requirements for a field instrument. It requires no external power source (battery-operated), is portable and features digital display of the signal either in microamperes or in ppm of chlorine after calibration.

Laboratory Performance of the Chlorine Flux-Monitor

Two series of experiments were conducted with the chlorine flux-monitor: (1) to assess its reliability in measurement of low levels of chlorine (2) to assess its accuracy.

(1) To study the performance of the chlorine flux-monitor in a laboratory assessible "natural" system, cold tap water was selected as the system to be investigated. A chlorine concentration was measured in undiluted tap water (after clearing the lines of stagnant water by running it for 1 hour before sampling). Subsequently, a factor of two dilutions of tap water with distilled water series was performed, and the concentration of chlorine was measured after each dilution. The results of this series of experiments are shown in Table 37.1.

(2) To test the accuracy of our measurement a fresh bottle of "Chlorox" was used to prepare 52 ppm stock solution. Subsequently this solution was diluted 1:1000 just before measurement and further diluted according to factor of 2 dilution scheme used in the tap water experiment. The results of this series of measurements are shown in Table 37.2.

Field Tests of Chlorine Flux-Monitor

Two separate field tests of the chlorine flux-monitor were performed. The first test was executed in an actual emergency situation at the peak of a massive fish kill near Newport News, Virginia. On May 30, 1974, during a fish kill our equipment was taken to Gloucester Point and used for monitoring chlorine in the James River. Our measurements were conducted aboard a boat furnished by the Water Quality Control Board (WCB) over several square mile areas of the river near the outfall of a sewage treatment plant. Initially our boat was the only one from which measurements were performed. Subsequently we were joined by another boat with a commercial amperometric titrator on board. The results of this river survey are as follows:

TABLE 37.1 Serial Dilution of Tap Water

Expt. No.	Dilution Factor	Calculated Conc. of Cl_2 ppm[a]	Measured Conc. of Cl_2 ppm	d
1	Undiluted	-	1.237	+0.002
2	2	0.618	0.620	-0.011
3	4	0.309	0.298	+0.006
4	8	0.154	0.148	+0.006
5	16	0.077	0.072	-0.005
6	32	0.038	0.038	0.000
7	64	0.019	0.020	+0.001
8	128	0.010	0.010	0.000
9	256	0.005	0.005	0.000
10	512	0.002	0.003	+0.001
11	1024	0.001	0.001	0.000
			$\bar{d}=$	± 0.003

[a] Based on the measured Cl_2 concentration in undiluted tap water in Experiment No. 1.

TABLE 37.2 Serial Dilution of Chlorox

Dilution of 52 ppm Chlorox Solution	Calculated Conc. of Cl_2 ppm	Measured Conc. of Cl_2 ppm	d
1:1000	0.052	0.051	-0.001
1:2000	0.026	0.025	-0.001
1:4000	0.013	0.011	-0.002
1:8000	0.006	0.005	-0.001
1:500	0.104	0.104	0.000
1:1000	0.052	0.053	+0.001
1:2000	0.026	0.026	0.000
1:4000	0.013	0.013	0.000
			$\bar{d}$ = 0.001

An electrochemical system for monitoring iodine concentration consists of a platinum microelectrode and a saturated calomel electrode. With 0 volt applied to such a cell one obtains a current proportional to the concentration of iodine (and thus chlorine).

For calibration purposes an accurately known amount of iodine can be generated coulometrically at a known rate. Consequently, the amount of electrochemically generated iodine, or known iodine flux, needed to produce an amperometric signal identical to the signal obtained from unknown water, corresponds to the unknown chlorine concentration.

Progress

Experimental Research

An analysis and calibration system was constructed taking advantage of the described electrochemical principles.

The electrochemical chlorine flux-monitoring system shown in Figure 37.1 was designed and constructed. It consists of two distinct and separate electrochemical cells, which function independently. Although the two cells are incorporated into a single system, each cell performs a unique function for which it was designed. The two cells are designated as follows: Calibrating generator (1); detector (2). In the system 0.1 M KI, pH 4 buffer in saturated NaCl solution is slowly injected into the stream (3).

Cell (1) operates only during calibration of the instrument, which can be performed as frequently as desired. The function of cell (1) is to generate a known, preselected, flux of iodine for signal calibration.

The chlorine monitor requires the aqueous solution (sample water) to flow at a uniform rate through the monitor (4).

The output of the detector cell (2) is electrical current, the magnitude of which depends on the concentration of chlorine. Typically for our system the current is 20 μA when the concentration of chlorine in the sample is 1 ppm.

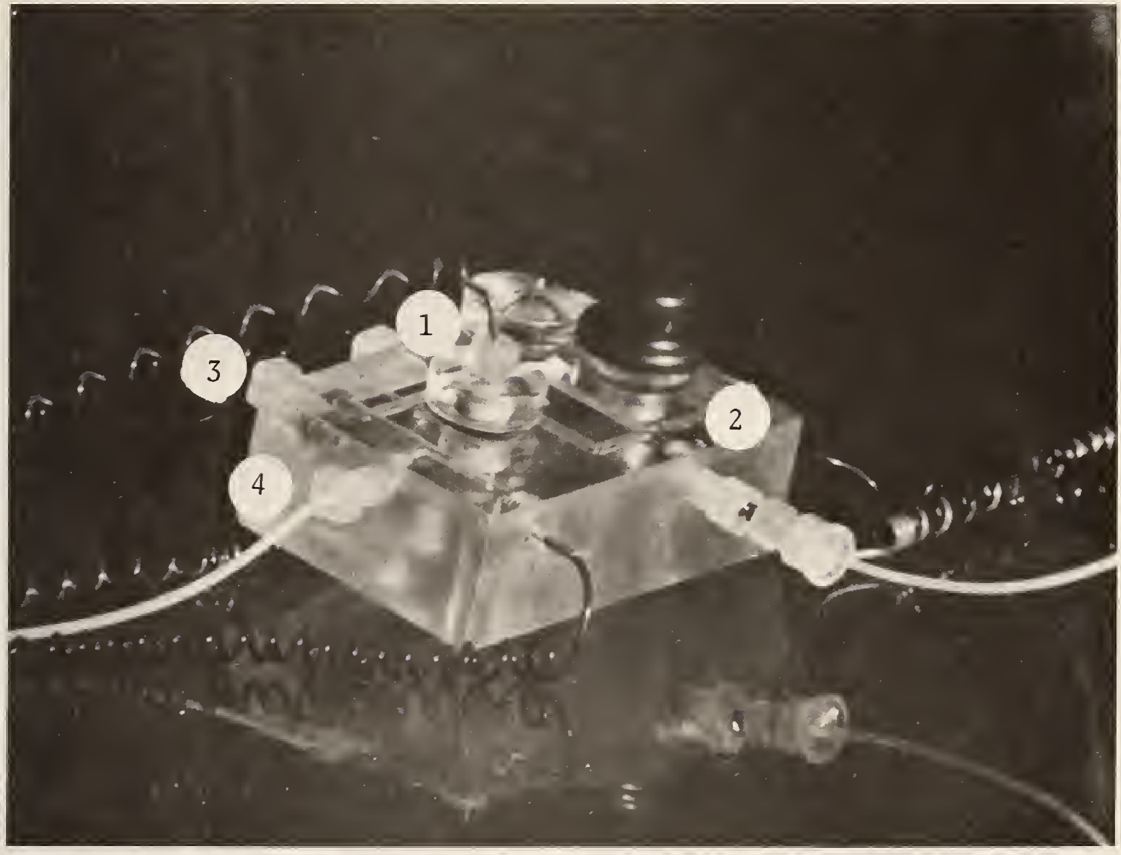


Figure 37.1 Chlorine Flux-Monitor
(1) Calibrating Generator Cell
(2) Amperometric Detector Cell
(3) Reagent Inlet
(4) Sample Inlet

June 30, 1974

Time, h	Location	NBS-VIMS Chlorine via Flux-Monitor,ppm	WCB Chlorine ppm
11:00	Outfall	0.160	--
11:20	Mid-River channel at Blunt Point	0.022	--
11:35	Bouy off N12	0.029	--
12:00	Outfall	0.223	0.20
12:20	Outfall	0.245	0.24
12:30	Outfall	0.252	0.23
12:55	200 m east of outfall	0.035	--
13:20	1000 m east of outfall	0.029	--
13:35	Outfall	0.181	0.21

At the request of the State of Maryland Water Resources Administration, the second expedition was made on June 19, 1974, to monitor chlorine in streams of Northern Maryland. A second instrument was also used in addition to the chlorine flux-monitor to determine the chlorine in the same water.

The fact that the chlorine flux-monitor has a small residual current due to the presence of iodine in KI-buffer mixture, for which compensation is made electrically and zero in the instrument, appears to be an asset. While the other titrator showed "zero" chlorine level in waters of most of the surveyed streams, our instrument showed a reversal in the polarity of the signal (negative sign) corresponding to 0.015 to 0.032 ppm chlorine equivalents of reducing agents in the water. This is additional significant data which is obtained using the flux-monitor. At one point we sampled the treated, undiluted sewage outfall from a small sewage treatment plant, which services a development in Northern Maryland. It was again an interesting test of the NBS chlorine flux-monitor. The amount of chlorine was too great to arrive at a confident value via the commercial instrument. Several burette fillings were required thus the estimate of chlorine level obtained via the other titrator was about 4.5 ppm. The virtually instantaneously responding NBS chlorine flux-monitor displayed 5.57 ppm as the concentration of chlorine.

A sample of stream water taken a few yards away from the outfall (consequently resulting in the dilution and reduction of chlorine by the stream water and the reducing agents present in the stream respectively) was also analyzed using the flux-balance monitor and the other titrator. The flux-monitor value was 0.028 ppm and that obtained using the titrator was 0.03 ppm.

The chlorine flux-monitor is an instrument which meets today's requirements of low level chlorine monitoring in natural waters. Experimental data show that chlorine levels of a few parts per billion can be measured with the uncertainty of 0.1 ppb.

Design and Construction of a Prototype Chlorine Flux Monitor

The aim of this part of the project was to design a self contained, portable chlorine monitor capable of field survey measurements utilizing the electrochemical cell devised by Dr. George Marinenko, and to produce eight of these instruments for field use and further evaluation.

A modular instrument was designed consisting of three assemblies: an electronic measurement and calibration unit, a rechargeable battery pack, and a water sampling unit containing the electrochemical cell. The design was based on information gained while using an earlier prototype electronic unit and from field and laboratory data. Special attention was given to providing increased sensitivity, stability and ease of operation.

Upon completion of the instrument design, two units were constructed and made available for operational tests. Subsequent evaluation including field tests conducted on the James River in Virginia in cooperation with the Virginia Institute of Marine Science revealed deficiencies in two areas of operation. The electronics malfunctioned when subjected to the extreme humidity of ocean air, the introduction of reagent was found to be inadequate and unreliable, and the reagent buffer mixture was unstable.

The electronics system has been modified to reduce or eliminate susceptibility to moisture. Stable operation under prolonged exposure to conditions of high humidity and temperature has been demonstrated. Operation in a salt air environment has yet to be shown. Acceptable operation of the reagent induction system has been achieved using separate ports for reagent and buffer with external capillary limiting flow.

In accordance with the production goal of eight units, all components have been acquired and assembled. The electronics systems for six units are complete and tested. Two water sampling units are complete and are undergoing tests with the remaining six units awaiting final design of the reagent introduction system.

A package of in-house drawings and documentation has been assembled and is being made available to all interested parties.

38. Priority Standard Reference Materials in Water Pollution

Project Leader: R. Alvarez, Office of Standard Reference Materials

Other Personnel: R. H. Meyer

Objective

To determine the most urgent Standard Reference Materials needs in water pollution.

Approach

A questionnaire was devised to determine the need for primary SRMs in water analysis, to provide guidance for their composition and production.

Progress

In all, 300 questionnaires were mailed to interested parties in industry, Federal, state, and local agencies, universities, private water testing laboratories, and centers for oceanographic studies. The mailing was directed primarily to members of the ASTM Technical Committee D-19 on Water. Information was requested under these headings:

I. inorganic pollutants
II. organic pollutants
III. turbidity or particulate
IV. anticipated use for all SRMs
V. information on low-blank reagents

A total of 165 responses have been received. The results of the responses are summarized in Tables 38.1 and 38.2.

TABLE 38.1 Relative Importance of Inorganic Pollutants and Desired Concentrations Based on Questionnaire Responses

	Concentrations in mg/liter (ppm)						
Mercury	0.001	1	0.005	0.05	0.01	5	10
Cadmium	0.01	0.001	1	0.1	0.05	5	10
Lead	1	0.05	0.01	0.1	0.001	5	10
Arsenic	1	0.01	0.001	0.05	0.1	5	10
Chromium	1	0.05	5	0.01	0.1	10	0.001
Copper	1	0.01	0.05	0.1	10	0.001	5
Cyanide	1	0.01	0.1	0.05	5	10	-
Selenium	0.01	1	0.001	0.05	0.1	5	10
Fluoride	1	10	0.1	0.5			
Zinc	1	5	0.1	0.01	10	0.001	0.05
Barium	1	0.1	5	10	0.01	0.5	-
Iron	1	10	0.01	0.1	0.05	-	-
Nickel	1	0.05	0.1	5	10	-	-
Silver	1	0.05	0.01	0.1	10	-	-

TABLE 38.2 Relative Importance of Organic Pollutants and Desired Concentrations Based on Questionnaire Responses

	Concentration in mg/liter (ppm)			
Polychlorinated Biphenyl	0.001	0.01	0.1	1
Aliphatic Hydrocarbons	1	10	0.1	
Aromatic Hydrocarbons	1	10	0.1	0.001
DDT	0.001	0.01	1	0.1
Aldrin	0.001	0.01	1	0.1
Dieldrin	0.001	0.01	1	0.1
Benzidine	0.001	0.01	1	0.1
Chlordane	0.001	0.01	1	0.1
Endrin	0.001	0.01	1	0.1
DDD	0.01	0.001	1	0.1
DDE	0.01	0.001	1	0.1
Toxaphene	0.001	0.01	1	0.1

39. Mercury in Water Standard Reference Material

Project Leader: H. L. Rook, I. L. Barnes, Analytical Chemistry Division
Other Personnel: J. Moody, P. Paulsen, and T. Rains

Objective

The objective of this project was to investigate stability, prepare and analyze trace ionic mercury in water solutions for ultimate SRM certification. Two mercury concentrations were chosen, one at ~1.5 µg/g for "spike" standardization of natural waters, and one at ~1 ng/g for benchmark standardization.

Approach

Tracer studies, using carrier free mercury-203 can reveal mercury losses from solution. Loss of mercury would be reflected in a diminishing gamma-ray count rate. Conditions would be sought under which no loss of mercury from solution would be experienced.

Progress

Solutions were prepared to a mercury concentration of 1.00 ng/ml, as the nitrate, and stored in 1 liter, precleaned, Teflon bottles. Carrier free mercury-203 was added to give a gamma-ray count rate of ~30,000 cm/min per ml of solution. One ml aliquots of each solution were withdrawn at successive time intervals and counted at a fixed geometry to determine the mercury concentrations.

Solutions were initially stabilized with acid or EDTA and studied for mercury loss as a function of time. The individual solutions were as follows:

1. 0.5 N HNO_3 + 1.0 ng/ml Hg^{++}
2. 0.5 N HNO_3 + 0.2 N H_2SO_4 + 1.0 ng/ml Hg^{++}
3. 0.001 M EDTA + 0.1 N NH_4OH + 1.0 ng/ml Hg^{++}

Loss of mercury from solution was found in all cases. The acid stabilized solutions lost about 20% per month (Figure 39.1 and the EDTA stabilized solution lost about 90% per month. After 16 days, 1 μg/ml gold, as the tetrachloride, was added to the solutions. The acid stabilized solutions recovered to the original mercury concentration and remained constant for the duration of the two-month study. The EDTA solution recovered to ~85% of its original concentration.

Following this study, two solutions were made, stabilized with 0.5 N HNO_3 and with $AuCl_4$ at the 0.01 and the 1.0 μg/ml levels, respectively. These solutions were stored in containers of Teflon, borosilicate glass, and polyethylene. To the present time, all solutions have maintained constant mercury concentrations within the error limits of the mercury-203 count rate.

I. Analysis

Analyses of the solutions were carried out by three independent analytical techniques: Atomic absorption, neutron activation, and isotope dilution spark source mass spectrometry. The major problem in the analyses was variation in the blanks of reagents and water used to make up the test solutions. Finally by using the NBS Analytical Chemistry Division-produced ultrapure water and reagents, and isolating all work to one clean area, the blank was reduced to about 0.05 ng/ml ± 100% relative. All analytical techniques improved their ability to determine trace mercury to the point where errors were less than ±5% total.

II. Production

1. Cleaning of Bottles and Ampoules--The glass ampoules used for the 0.5 ppm SRM were first cleaned by multiple rinses with distilled water followed by immersion in a bath of boiling 1 + 5 HNO_3 for 24 hours. After draining out all of the acid and rinsing with distilled water, all of the ampoules were filled with a special ultrahigh purity distilled water prepared at NBS.

A period of two weeks storage was allowed for the water to leach the ampoules. Afterwards they were drained, rinsed with ultra-high purity water and then dried in a class 100 forced clean air oven. The Teflon bottles were cleaned in a similar manner with 1 + 5 HNO_3 followed by 2 or more weeks storage with ultra-high purity water in them. The Teflon bottles were air dried in a clean room, numbered, and then weighed dry.

All other plastic containers, volumetric flasks, pipets, and other apparatus received a similarly thorough cleaning. All apparatus and containers were new, having never been used for mercury before. All water and acids used in the preparation of the solutions were ultra-pure reagents made by a sub-boiling distillation process at NBS.

2. Preparation of Solutions--Weighed amounts of pure gold and pure mercury were dissolved and made to volume in volumetric flasks using ~6 N HNO_3. A master solution for the 1.5 ppm standards was prepared by weighing out the appropriate amounts of HNO_3 and H_2O to give 20 liters of 0.5 N HNO_3 in a clean polyethylene carboy.

On the day before the ampouling operation for the 1.5 ppm standard, aliquots of the gold and then mercury solutions were added to the carboy. A magnetic stirrer was used to keep the solution well mixed.

The dilute master solution for the 1.2 ng/g standards was prepared by diluting the primary mercury standard. This was done by weight in a clean two-liter Teflon bottle.

All of the one liter Teflon bottles for the 1.2 ng/g standard were individually filled with 940 ml of water with sufficient nitric acid added to make the solution ~0.5 N in HNO_3. Approximately 10 μg of gold was added to each bottle. This operation was also done on a weight basis.

3. Production--An ampouling machine with Teflon tubing and valves and a glass piston pump was used to fill the glass ampoules with the 1.5 μg/g master solution. All liquid contact parts were thoroughly cleaned in HNO_3 and after assembly the entire system was purged by pumping several hundred ml of the master mercury solution. During the automatic ampouling operation, a class 100 clean air environment was maintained around the apparatus. All ampoules were sequentially numbered for sampling purposes.

For the 1.2 ng/g SRMs, a 10 ml aliquot of the dilute master solution was added to each of the one liter Teflon bottles which had been previously filled with 940 ml H_2O + HNO_3 and the gold stabilizing agent. Since this solution was also prepared by weight, several determinations were made of the final solution density in order to convert weight concentration values to volume concentration values. The theoretical concentration of mercury in these two SRMs was calculated to be 1.495 μg/g and 1.23 ng/g, respectively in a nominally 0.5 N HNO_3 solution. The nominal gold concentrations were 1 μg/g and 10 ng/g, respectively.

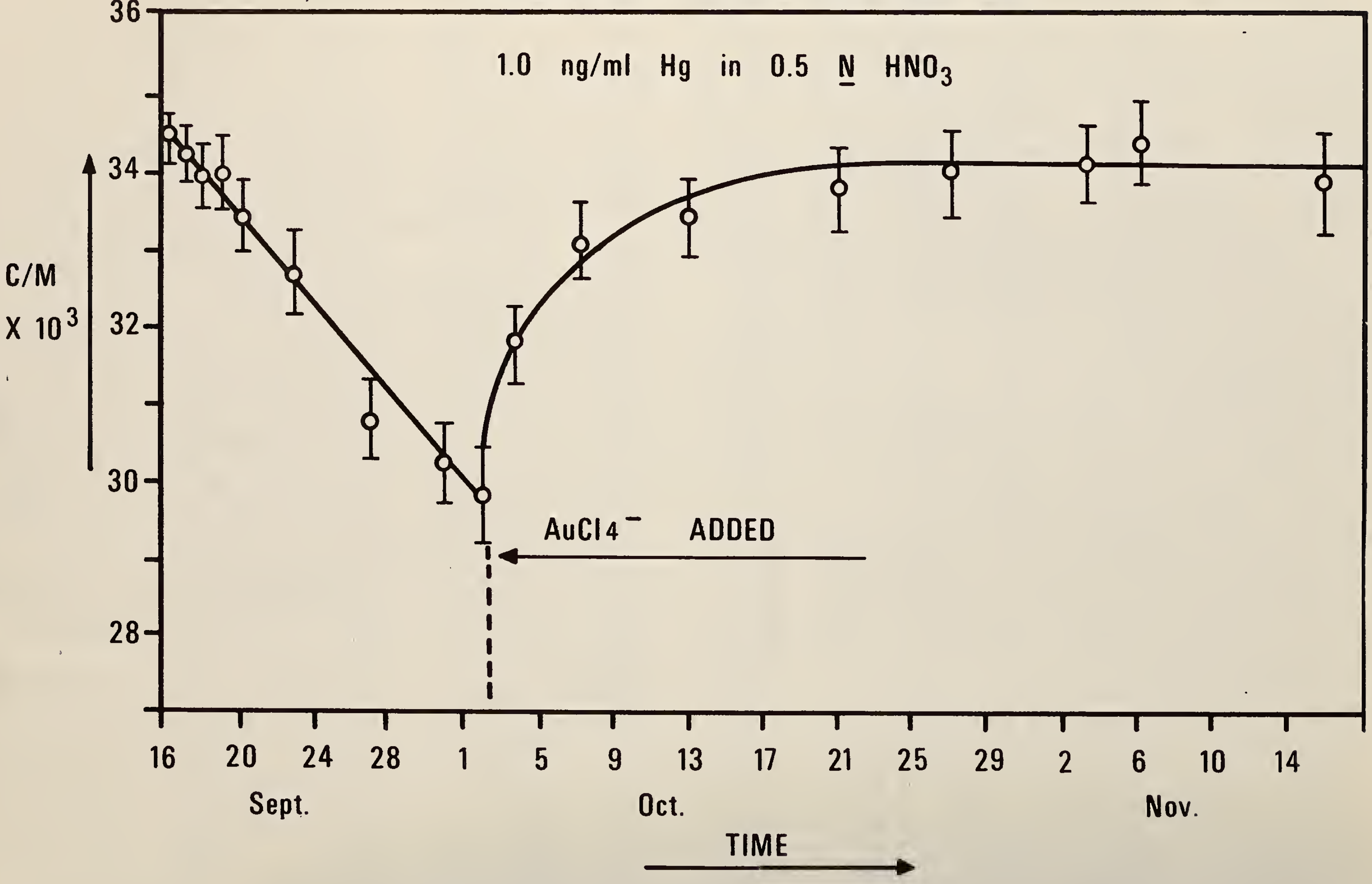
All work on SRM #1641 and 1642, Mercury in Water Standard, is complete. A successful method for stabilizing ng/g levels ionic mercury in water was developed. Analytical methods for the determination of mercury at that level were studied and improved. Final certification analyses were completed within the ±5% error limit originally desired. The certified mercury contents are:

SRM #1641 - 1.49 ± 0.02 μg/g

SRM #1642 - 1.18 ± 0.04 ng/g

Figure 39.1

MERCURY LOSS IN WATER



40. Mercury in Water Collaborative Study

Project Leader: D. A. Becker, Analytical Chemistry Division
Other Personnel: I. L. Barnes, J. R. Moody, H. L. Rook,
P. J. Paulson, T. C. Rains

Objective

To determine the present state-of-the-art for the determination of mercury in water at ambient concentrations, and to evaluate the effect of a Mercury in Water Standard Reference Material (SRM) on the analytical results obtained by a variety of laboratories.

Approach

Two Mercury in Water SRM's have recently become available from NBS, a low level SRM (1642) certified at 1.18+0.05 ng/g, and a higher level SRM (1641) intended for laboratory spiking or dilution wich is certified at 1.49+0.05 μg/g. These solutions were stabilized with gold ions as described. [1]. In an attempt to evaluate the effect of these new SRM's on the measurement system as it presently exists for mercury in natural water, a set of four stabilized mercury solutions were made at varying concentrations, ranging from less than one-half to almost five ng/g. Seventeen laboratories were statistically randomly selected from a group of over thirty which expressed an interest in participating in this study. The laboratories selected included four federal government laboratories, seven city and state government laboratories, and six industrial, non-profit, or private testing laboratories.

Progress

The study was completed in two steps. The first step, undertaken prior to the general announcement to the availability of the SRM's, entailed sending 250 ml samples of the four test solutions to the laboratories for analyses. They were to apply their standard analytical technique for natural waters (including digestion), using not more than one-half of each sample. The second step included reanalysis of the remaining portion of the samples, but was to be completed only after each of their analytical systems had been evaluated and optimized using SRM 1642, Mercury in Water-Trace. The study has now been completed, and twelve of the laboratories have submitted their final results. These results have been statistically evaluated as to general mercury analysis capabilities and the effect of SRM use on the final values.

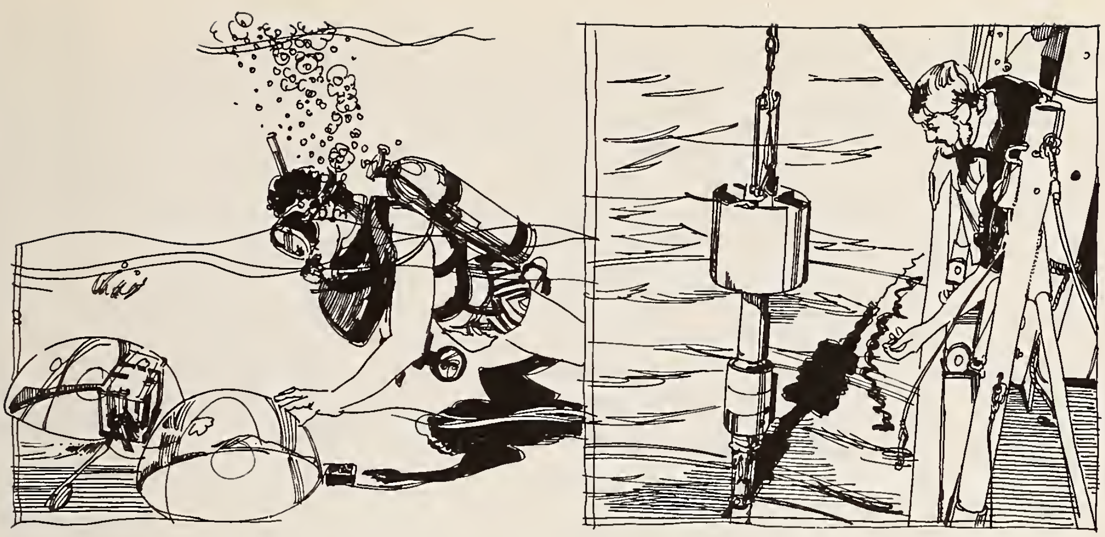
Results and Discussion

The date received showed a great deal of scatter, with several of the laboratories submitting individual values in error by a factor of 10 or more. Of the twelve laboratories reporting results, only eight provided unambiguous information on all concentration levels. The results from these eight laboratories were then evaluated statistically for each of the four concentration levels. The analytical precision (relative standard deviation, expressed as the percent of the average) ranged from 60% at approximately 0.2 ng mercury/g solution, down to almost 7% at the 5 ng/g concentration level. The analytical accuracy without the SRM (expressed as percent deviation from the "known" target value) ran from +33% at the 0.2 ng/g level, down to +4% at the 5 ng/g level. The accuracy of the results by the laboratories after using the SRM to calibrate their instruments was only slightly improved, ranging from +28% down to +3%.

The conclusions which must be drawn from the above results are that the present state-of-the-art for the determination of mercury in water at the ng/g concentration level is so imprecise that it was difficult to evaluate the effect of the Mercury in Water SRM at these levels. This is illustrated by the fact that for the eight of seventeen laboratories which were able to complete the analyses satisfactorily, the imprecision of all determinations below 1.0 ng/g averaged ±57%.

References

[1]. Rook, H.L., and Moody, J., Stabilization and Determination of Nano-gram Quantities of Mercury in Water, Proceedings of *Nuclear Methods in Environmental Research*, University of Missouri-Columbia (July 1974) pp. 44-53.



41. Transformations of Heavy Metals in Aquatic Environments

Project Leaders:	F. E. Brinckman, Inorganic Materials Div. and W. P. Iverson, Metallurgy Div.
Other Personnel:	G. E. Parris, K. L. Jewett, W. Blair
Guest Workers:	C. W. Huey, J. M. Bellama, T. Watters, and D. Nies, University of Maryland; Br. J. E. Doody (Christian Univ., Tenn.)

Objective

The principal objectives of this continuing project are to characterize the sources and fate of toxic heavy metals in the environment through: (1) determination of key biological, chemical and physical mechanisms in natural water systems for mobilization and transport of heavy metals, and (2) development of measurement capabilities for this characterization. Information derived from new instrumental approaches to these studies can provide keys for the prevention or control of release of toxic, methylated forms of such heavy metals from new sources such as antifouling coatings or pesticides or already established reservoirs in natural bodies of water (rivers, estuaries, etc.).

Approach

An understanding of the chemical and biological nature and dynamics of metals transport in natural waters requires a balanced interdisciplinary approach to characterizing key pathways. The NBS interdivisional team comprises organometallic and microbiological expertise.

The effort has involved some outside sponsorship from the Environmental Protection Agency, the Naval Ship Research and

Development Center, and the National Science Foundation. Support in the form of available shiptime from NSF and the Chesapeake Bay Institute has permitted continuance of an active field sampling program in the Chesapeake Bay. Academic collaborations also form an integral component of this interdisciplinary project. Thus, joint research continues with Dr. Colwell of the Marine Microbiology Group and Guest Workers and staff from the Chemistry Department at the University of Maryland. Collaboration with the Virginia Institute of Marine Science (VIMS) has also been ongoing during the period. Such involvement ensures a realistic and balanced approach to relevant metal transport questions involving both chemical and biological processes.

Progress

41.1 Instrumental Development

An instrumental method for the determination of metallic mercury, dimethylmercury and methylmercury in the nanogram range has been developed and placed into routine laboratory use [3]. This method employs a gas chromatograph coupled with a mercury-specific flameless atomic absorption spectrophotometer (GC-AA) which serves as the detector for elemental mercury or organomercurial species eluting from the chromatographic column. The method has been used for qualitative surveys of trace organomercurial compounds produced from biological and abiotic processes as well as for the indirect detection of methylated forms of other metals which can exchange methyl groups with mercury(II) (Fig. 41.1.1).

For the specific detection at trace levels of volatile forms of metals other than mercury, the GC was coupled to an atomic absorption spectrophotometer employing a graphite furnace (GC-GF-AA). The effluent from the GC was passed *via* a thermostatically controlled stainless steel transfer tube to the graphite furnace (Fig. 41.1.2). Since the maximum time to which the graphite tube could be heated at the atomizing temperature is limited, a solid state electronic logic circuit was built and incorporated into the NBS GC-GF-AA unit to permit pulsing the furnace (viz.; 30 seconds on 15 seconds off) as the GC effluent passed through it (Fig. 41.1.3). Pulsed gas chromatograms of tetramethyltin and tetraethyltin are indicated in Fig. 41.1.4).

More recently, the GC-GF-AA system has been evaluated for the quantitative element-specific analysis of gaseous Me_3As, Me_2Se, and Me_4Sn, ($Me=CH_3$), as well as for their detection in aqueous media. The atomization temperatures were found to be reasonably predictable from available thermochemical properties of the elements and compounds

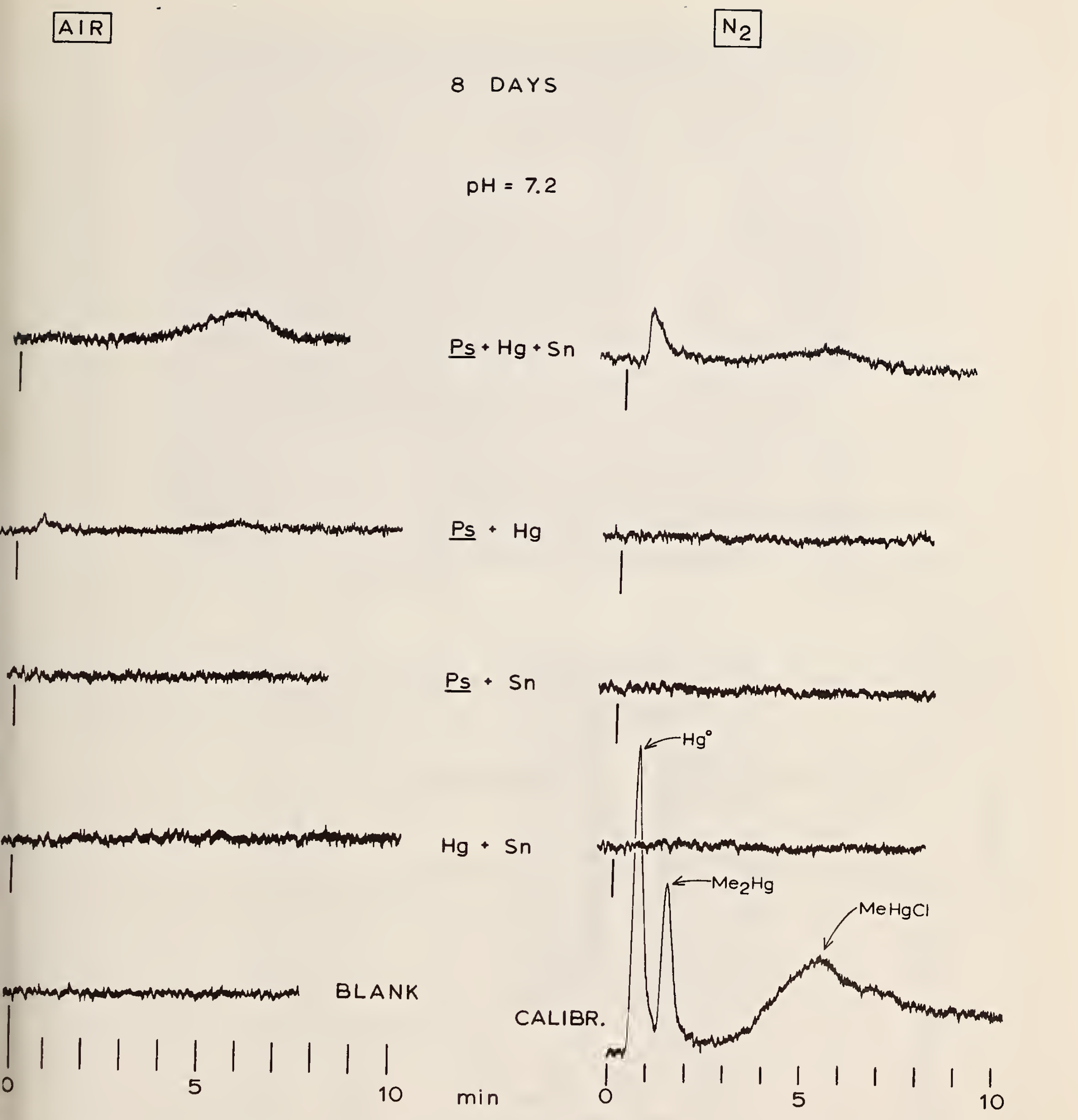


Figure 41.1.1 Pseudomonas grown on metal-doped slants under either air or nitrogen atmospheres after eight days.GC-AA spectra show substantial reduction in free mercury content of air-grown series,but a large concentration of methylmercury has formed in those vessels where Pseudomonas is exposed to both Hg(II) and Sn(IV). In the corresponding anaerobic series under N$_2$, substantive amounts of both gaseous mercury and methylmercury form, although the calibration spectrum at bottom confirms the absence of dimethylmercury.

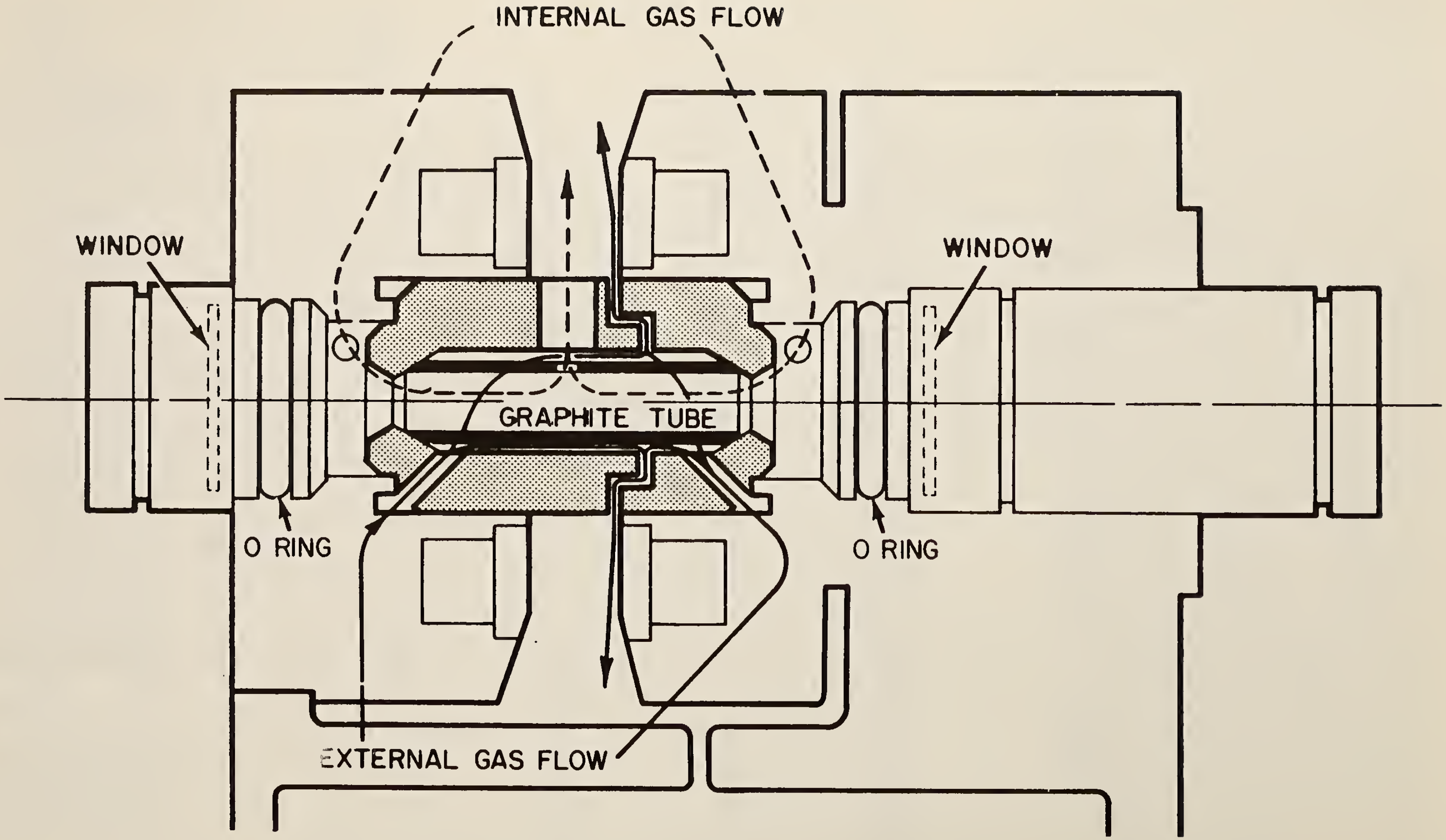


Figure 41.1.2 Cross-section diagram of graphite furnace detector for GC-GF-AA, showing eluent gas flow from GC (dashed lines).

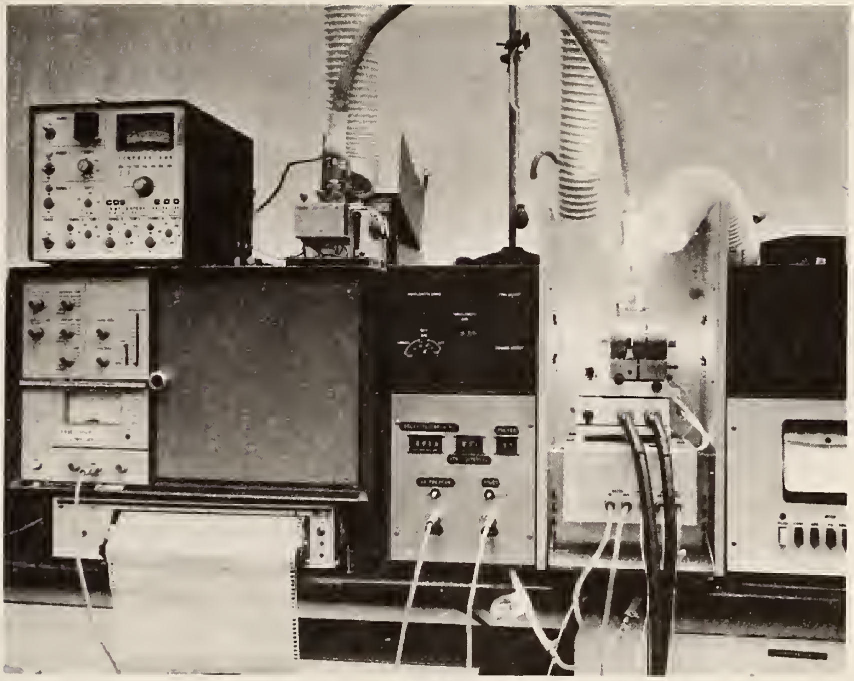


Figure 41.1.3 Gas-chromatograph (left) coupled to an atomic absorption unit(right) via thermostatically controlled tube (above both units) and electronic pulse programmer (lower center).

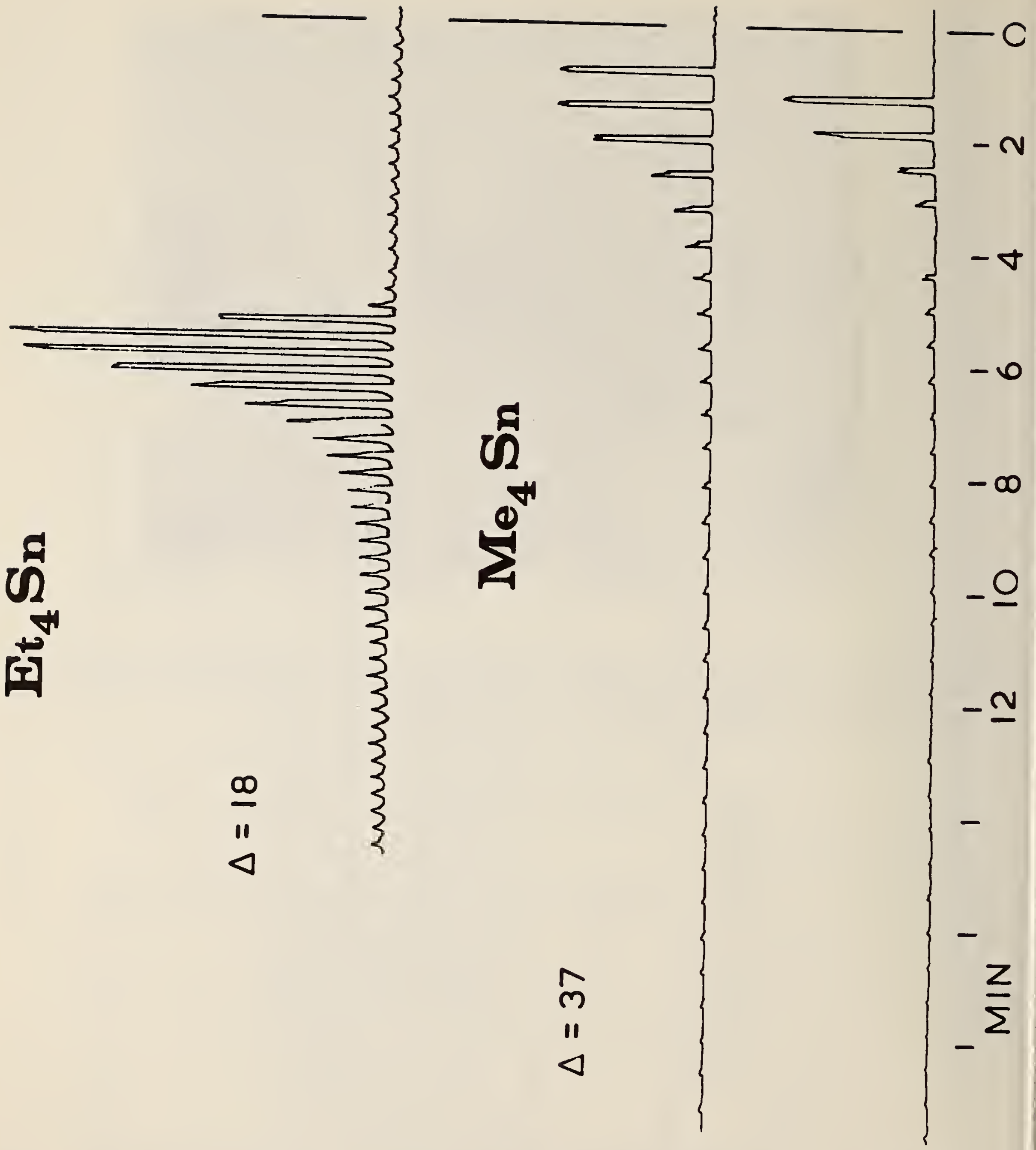


Figure 41.1.4 Pulsed AA-chromatograms of gaseous samples of tetramethyltin and trimethyltin are compared, showing Sn-specific detection at λ = 224.6 nm. Δ represents interval between atomization pulses at 2700°.

(Table 41.1.1). Thus, a consideration of the critical reactions occurring during atomization in the graphite furnace (Fig. 41.1.5) suggested improved AA techniques. It was found that the sensitivity could be greatly increased by the addition of H_2 to the GC carrier gas, thereby using considerably reduced atomization temperatures (1500-1800 C°) allowing the elimination of the pulse mode of operation, just described, for such less refractory organometallic compounds. This dramatic improvement is illustrated in Figure 41.1.6. Typical calibration curves for Me_2Se, Me_3As, and Me_4Sn are shown in Figure 41.1.7. Specific analytical details are presented in Table 41.1.2. along with evaluation of detection limits at 95% confidence limits. Details of this work are in the process of being prepared for publication [13]. The GC-GF-AA facility currently permits serial metal-specific detection of such organometals at nanogram concentrations in head gases above water containing a variety of organic compounds associated with bacterial metabolites. The system is clearly applicable to other volatile organometals at trace concentrations. Preliminary results for organosilanes appear promising, although so far column decomposition has limited effectiveness for speciation and quantification of very highly reactive organometallic gases, such as dimethylcadmium.

A Perkin-Elmer Model AD-2 electronic microbalance has been acquired which facilitates the weighing of small solid samples for direct solids analysis with the AA unit.

41.2. Field Studies and Sampling

During the past three years, an active field schedule of sediment, water and plankton sampling of the Chesapeake Bay has been pursued. Materials so acquired have formed the basis of most of the specific laboratory experimental parts of the project, *e.g.*, isolation of bacteria and analysis for sulfur, metals, and oil.

Investigation of elemental sulfur found in the Chesapeake Bay sediments revealed an enrichment of S^{32} over S^{34} in all except one of five sulfur samples, indicating bacterial sulfur cycling. In these sediments, as much as 50% of the total mercury loading was found to be available in a soluble (organic solvents) form, bound to complex organic groups. The Hg in petroleum fractions from the sediment was detected by Hg-specific GC-AA in oil fractions eluting at retention times characteristic for either C_{20} petroleum components or organomercurials of high molecular weight (Figure 41.2.1)[8].

Availability of the new GC-GF-AA facility will now permit extension of this Hg-speciation work to evaluation of other metal species in marine sediments. Of particular interest

Table 41.1.1

Calibration Curves for GC-AA Analyses of Trace Organometal Gases in Nitrogen

Organometal[a]	Concentration Range, ng	N	r	Slope, m(± % std error)[b]	Intercept, a(± % std error)[c]	R.S.D.,%[d]	Sensitivity, ψ, μg^{-1}[e]	Detection Limit, δ, ng[f]	Conditions[g]
Me_3As	0-320	30	0.965	606,888 (5.13)	-6,465 (77.2)	33.2	516	5	1800°,G, H_2
Me_3As	0-512	28	0.975	757,800 (4.48)	-20,279 (3.30)	44.3	197	14	1800°, P, H_2
Me_3As	0-384	34	0.995	798,021 (1.83)	+13,317 (19.6)	11.5	327	8	1500°, S, H_2
Me_3As	128-1152	13	0.930	218,456 (12.0)	-18,669 (94.4)	910	7.6	288	1700°, S
Me_3As	128-1024	8	0.979	130,726 (8.56)	+5,776 (134)	50.9	13.6	180	1700°, S
Me_3As[h]	64-1284	25	0.949	296,958 (6.90)	-56,537 (26.9)	122	9.1	228	Pulsed, 2700°, G
Me_3As[i]	64-1280	25	0.936	176,777 (7.84)	-39,485 (26.1)	102	8.0	259	Pulsed, 2700°, G
Me_2Se	0-391	27	0.987	793,756 (3.27)	+11,468 (32.6)	16.7	297	9	1500°, S, H_2
Me_2Se	0-313	29	0.997	1,285,109 (1.56)	+5,047 (44.4)	7.0	386	7	1800°, G, H_2
Me_4Sn	0-363	29	0.988	508,990 (3.08)	+1,077 (237)	18.6	223	12	1800°, G, H_2
Me_4Sn	61-484	14	0.972	425,829 (7.04)	-19,858 (42.7)	72.3	25.9	83	1500°, S, H_2

---

[a] *Ca.* 200-400 ppm gaseous organometal in ultra-pure N_2; typically 0.05 to 1.0 cm^3/g samples taken for GC-AA run

[b] In units of $\mu V \cdot s \cdot \mu g^{-1}$.

[c] In units of $\mu V \cdot s$.

[d] Calculated at 0.1 μg metal.

[e] See reference [18].

[f] See reference [20].

[g] Ar gas flow from GC at 20 ml min^{-1}, with *ca.* 1-2 ml min^{-1} H_2 added as noted. G = graphite furnace tube along; S = graphite tube fitted with SiO_2 liner; P = graphite tube coated with pyrolytic carbon.

[h] Calculated by Method I, see text.

[i] Calculated by Method II, see text.

Table 41.1.2

Thermodynamic[a] and Kinetic Data Relevant to AA Detection of Selected Organometals

Compound	b.p. (° C)	A[b]	E_a[b,c] (kcal/mole)	Decomposition[d] Temp (° C)	Element b.p. (° C)	Dissociation[e] Energy M_2 (kcal/mol)	Dissociation[f] Energy M-H (kcal/mole)
$(CH_3)_2Zn$	44	11.2[g]	47.2[g]	635	907	7	20
$(CH_3)_2Cd$	106	11.9[h]	45.8[h]	556	765	3	16
$(CH_3)_2Hg$	93	13.1[h]	50.1[h]	553	357	4	9
$(CH_3)_3As$	52	12.8[i]	54.6[i]	648	(subl) 613	92	65
$(CH_3)_3Sb$	80	15.2[j]	57.0[j]	538	1380	71	
$(CH_3)_3Bi$	110	14.0[j]	44.0[j]	406	1560	45	59
$(CH_3)_4Sn$	77				2260	47	63
$(CH_3)_4Pb$	110				1744	24	42
$(CH_3)_2Se$	55				685	80	73
$(CH_3)_2Te$	94				1390	63	64

[a] Reference [24].

[b] $\mathrm{Log}_{10}\ (k/s^{-1}) \cong A - (Ea/2.303\ RT)$

[c] E_a M-CH_3 bond dissociation energy

[d] Temperature at which t 1/2 = 1 s, rate constant = 0.693 s^{-1}

$$T = \frac{E_a}{(0.159 + A)\ (4.576 \times 10^{-3})} - 273$$

[e] For $A_2 \rightleftarrows 2A$, ΔG = dissociation energy - T (31×10^{-3} kcal/mole)

[f] H_2 bond energy is 104 kcal/mole

[g] Reference [26]

[h] Reference [27]

[i] Reference [28]

[j] Reference [29]

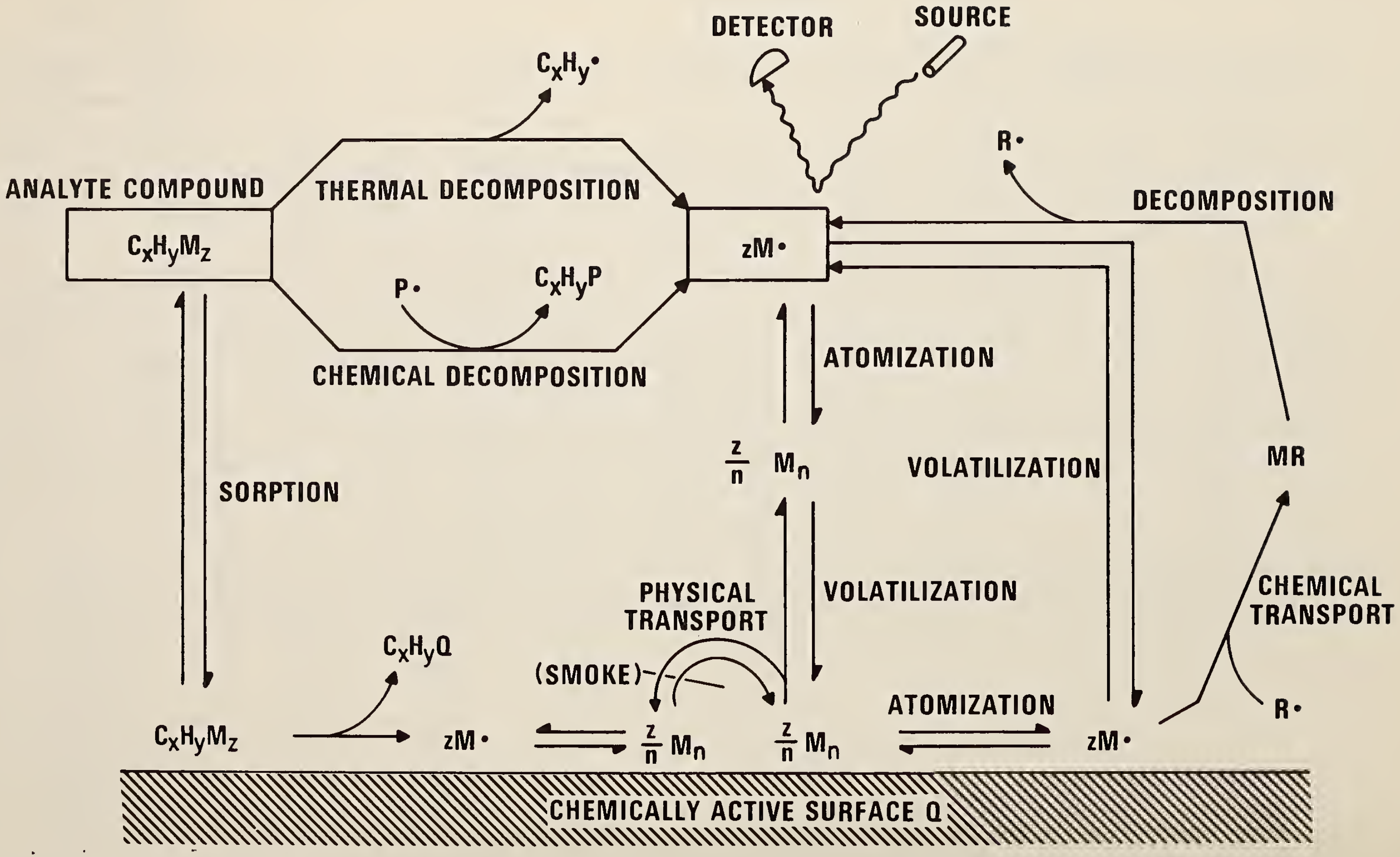


Figure 41.1.5 Some of the major reactions and equilibria presumed to be involved in the GC-GF-AA system. (cf. Table 41.1.1).

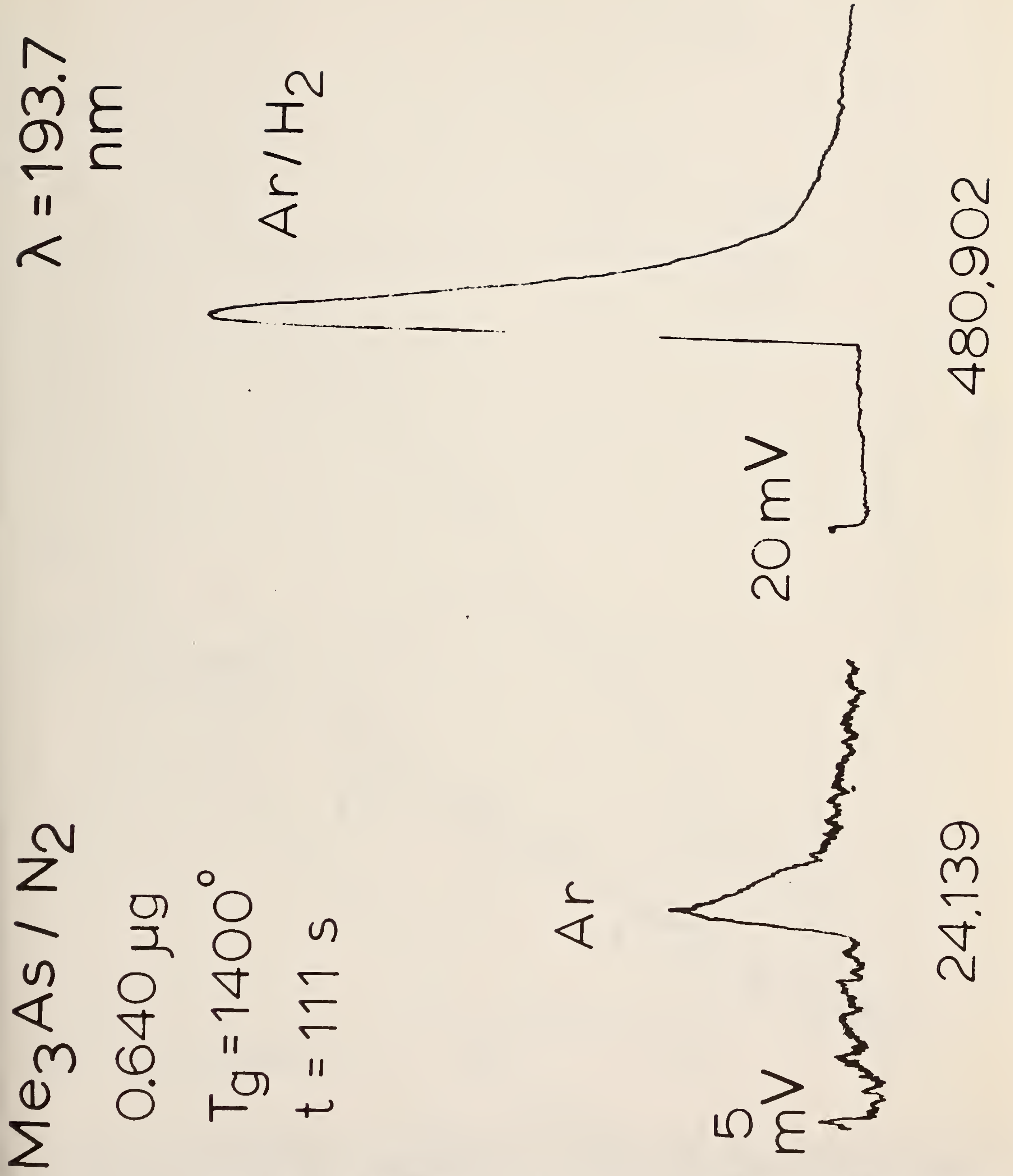


Figure 41.1.6 Comparison of atomization efficiency curves for trimethylarsine in a silica-lined graphite furnace with and without hydrogen added to the carrier gas. Relative GC peak areas are indicated below the curves. Similar results are observed using other furnace surfaces. Above ∿1800° on bare graphite, the effect of hydrogen is relatively small since arsenic is efficiently atomized without H_2.

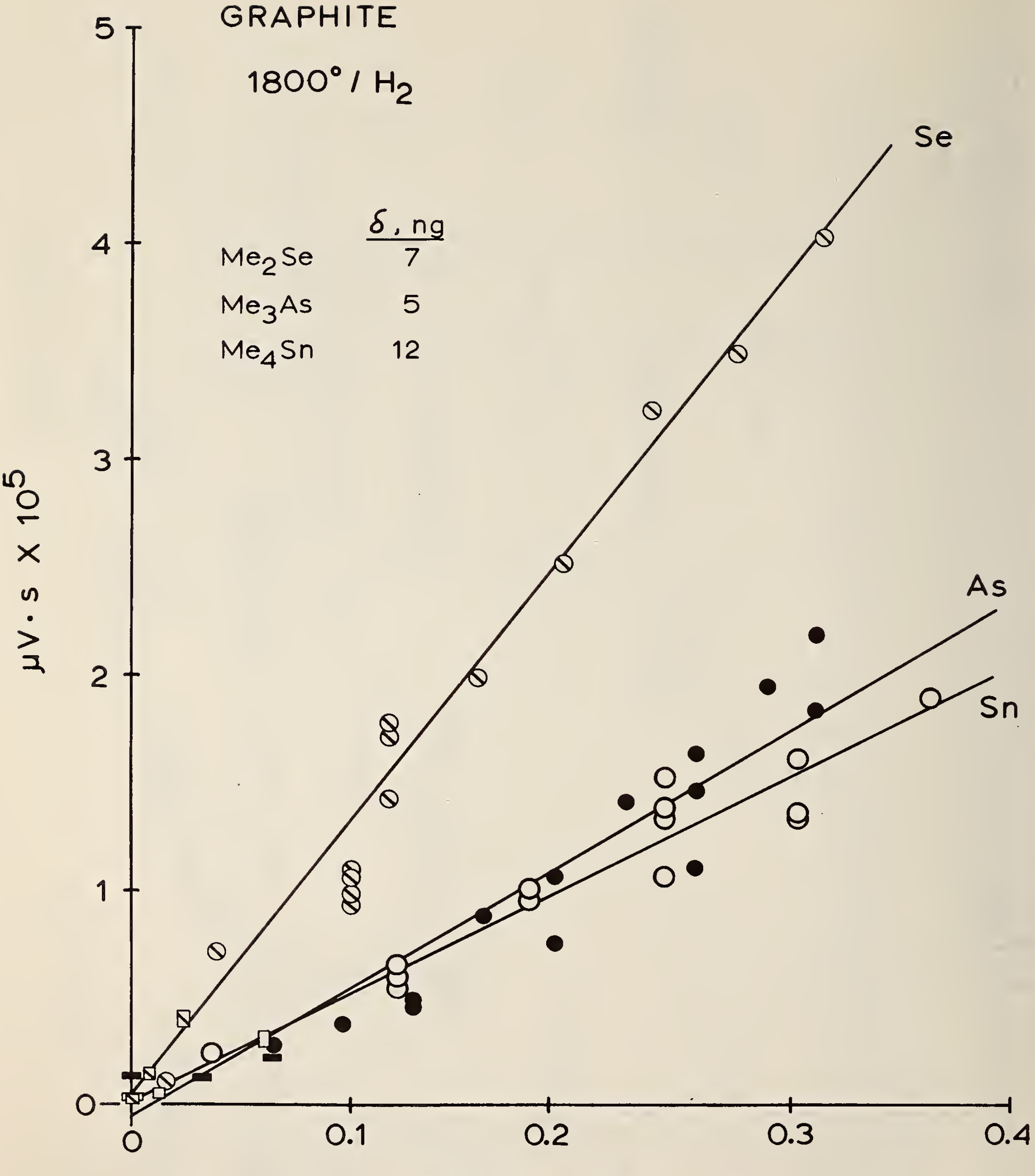
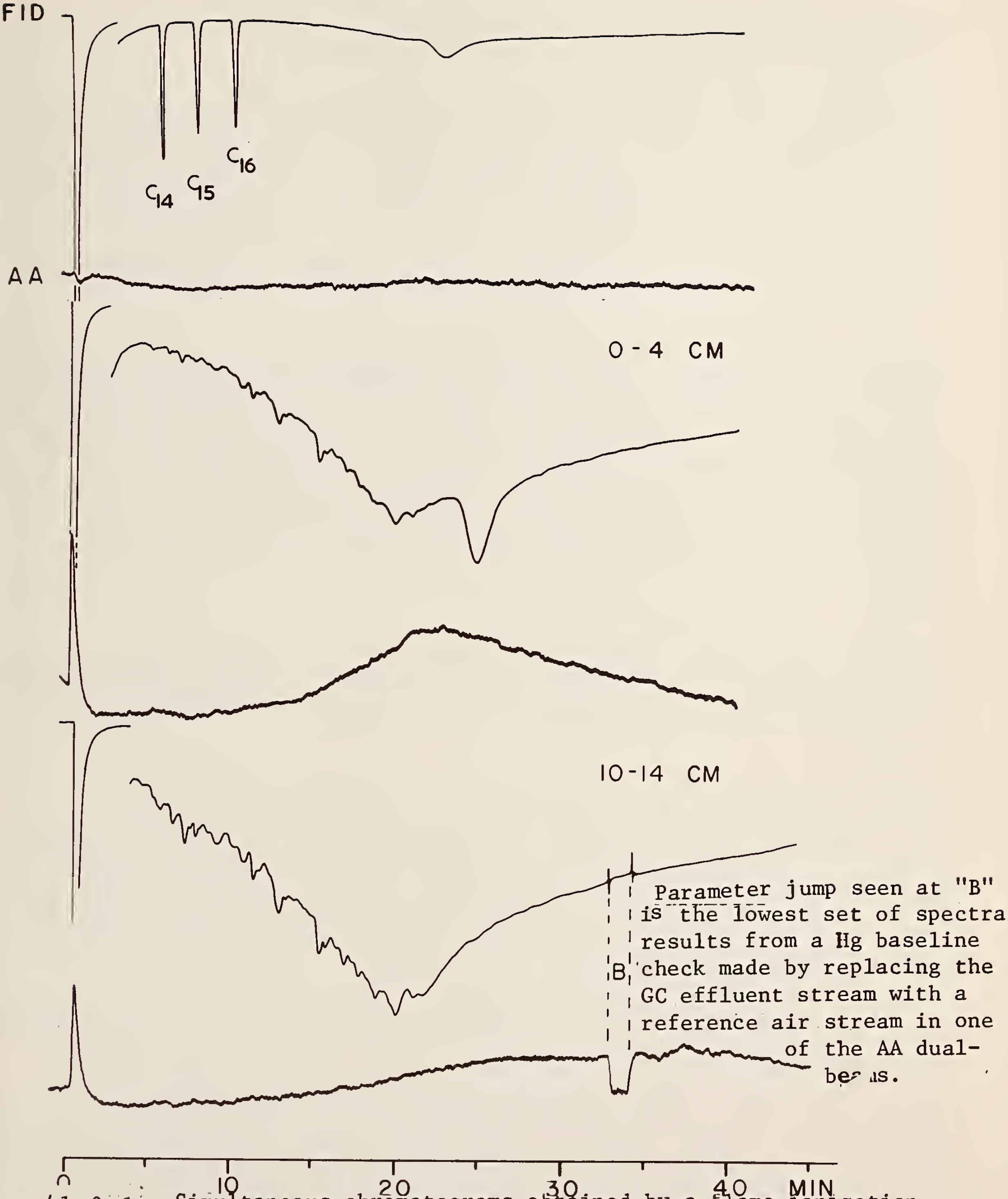


Figure 41.1.7 Calibration curves are compared for trimethylarsine, dimethylselenium and tetramethyltin in a graphite furnace at 1800° with 10% H_2 added to carrier gas. Each rectangle shows the results of five consecutive injections; these data were used to determine detection limits and sensitivity of the measurement (cf. Table 41.1.2) The organometallic gases were introduced into the GC-GF-AA system as various size injections of a standard gas mixture in ultrapure N_2.



Parameter jump seen at "B" is the lowest set of spectra results from a Hg baseline check made by replacing the GC effluent stream with a reference air stream in one of the AA dual-beams.

Figure41.2.1 Simultaneous chromatograms obtained by a flame ionization detector (FID) and a mercury-specific flameless atomic absorption detector (AA) are compared for a known, Hg-free calibration mixture of C_{14}-C_{16} paraffins (top) and oil extracts from two sections of a Colgate Creek core. The 0-4 cm sample contained total Hg=0.7μg/g with 45% as extractable Hg, plus .8% free S°; the 10-14 cm sample contained total Hg=0.7μg/g with 26% as extractable Hg, plus 1.1% free S°. Significantly different retention times of ca.22 and 36 min. were noted for the ligated mercury effluents.

will be the speciation of petroleum (or lipid) bound metals such as lead, tin, arsenic, and cadmium.

In a trial experiment to determine the presence of methylmercury volatilized from the Chesapeake Bay sediments, the GC and mercury specific atomic absorption units were installed aboard the Johns Hopkins Research Vessel Ridgley Warfield. Evidence for the formation of at least two unidentified volatile species of mercury (other than Hg°, methyl- and dimethylmercury) from fresh sediment alone and sediment mixed with a strain of Pseudomonas, was obtained directly in the field.

Samples of frozen, unidentified plankton from the Chesapeake Bay were sent to us for speciation of the incorporated mercury. Unfortunately, the sample size was too small to permit valid characterization of the Hg species. In future studies, on the identification of mercury species in samples of biota, a programmable micropyrolyser, received during this report period, will be used to pyrolize biological samples on-stream preliminary to GC-AA analysis, hopefully liberating the volatile mercurials (or other organometals) from the complex matrix.

Oyster slime from fresh specimens provided from VIMS, was found to produce only Hg° from Hg(II). No methylmercury was detected as had been by Jernelov (Swedish-Finnish Mercury Symposium, Helsinki, 1967).

A field study was conducted to investigate the effects of Sn(IV) on the uptake and transport of Hg(II) by water, sediment, and biota near an underwater habitat (ca 1 mile from Grand Bahama Island). This occurred as a result of our collaboration with VIMS and their working relationship with NOAA which operates the habitat. Collected samples have been kept frozen at -80 C° and will be analyzed for tin and mercury employing the GC-GF-AA facility.

A box-type sediment sampler which permits taking top sections of undisturbed sediment was purchased. Plans were obtained for the construction of an underwater sediment gas sampler and this unit is now under construction in NBS shops. This combination of refined field samplers will bring a more sophisticated and reliable approach to the NBS field sampling program. In particular, it is planned to apply NBS laboratory GC-GF-AA capability to both determination and speciation of selected toxic heavy metals transported across sediment-water interfaces.

41.3 Biological Metal Transformations

It has been well established that a number of transformations of heavy metals can be carried out by microorganisms, chiefly bacteria and fungi [1,2,3,4,6]. Since these microorganisms form a major part of the biota in natural environments, an evaluation of their metal transforming abilities is necessary to evaluate the potential importance of these activities in bringing about metal transformations.

41.3a Mercury

Employing the GC-AA method, a number of bacterial isolates from the Chesapeake Bay were found to produce primarily volatile metallic mercury from Hg(II), but a few demonstrated a capacity to methylate the metal as well. Utilizing hermetically sealed bioreactors with the GC-AA detection system [1,3] the effects of aerobic versus anaerobic conditions on several of the facultative isolates was demonstrated for the first time to influence the form of mercury transported. Thus the methylating capacity of these isolates was found to be associated with anaerobic conditions, whereas the same organisms could produce only metallic mercury in air.

Bacterial methylation and Hg° formation from Hg(II) by two strains of the common intestinal bacterium, *Escherichia coli*, were demonstrated. These strains have been extensively used in molecular biological and genetic studies.

41.3b Tin

A mercury-tolerant strain of *Pseudomonas*, isolated from the Chesapeake Bay, was demonstrated to also tolerate inorganic Sn(IV), Sn(II), and Cd(II) salts, as well as a number of other heavy metal ions [10]. In the presence of Hg(II) salts, incorporated into Nelson's agar medium (an artificial estuarine salts solution containing glucose yeast extract, and hydrolyzed casein), elemental mercury was produced by the organism. On this medium containing Sn(IV), the organism generated a volatile methylated tin species.

Evidence for the formation of the volatile tin species was based on a spectrofluorimetric technique employing flavinol as the ligand and on mass spectrometric and atomic absorption evidence [6,7]. Growth of this mercury-tolerant strain of *Pseudomonas* in the presence of both Hg(II) and Sn(IV) resulted in the formation of methylmercury (Fig. 41.1.1).

A postulated mechanism to account for this novel formation of methylmercury is:

$Sn^{4+} \rightarrow$ Methyltin species (Biological pathway)

Methyltin species $+ Hg^{2+} \rightarrow MeHg^{+}$ (Abiotic reaction).

In view of recent data [8,16] indicating a strong correlation between tin and mercury in river sediments and aquatic plants, the availability of this information will affect future models for bimetallic environmental interactions and urgently suggests new lines for environmental chemistry in the future.

41.3c Cadmium

A joint NBS-EPA project was initiated in order to assess the environmental mobility of cadmium in aquatic systems and to develop means for speciation of important transport species. The involvement of a natural product, Vitamin B_{12}, in its common form as cyanocobalamin, has been shown to provide specific stimulation to the same metal-resistant marine bacterial isolate resulting in volatilization of cadmium from its inorganic salts [14]. The experiments have been controlled in a number of ways which verify the need for the microorganism, *Pseudomonas sp*, plus Cd^{2+} and the cobalamin in a well-established laboratory estuarine salts nutrient medium (Figure 41.3.1). No cadmium is detectable (~0.01 ng level) in a sterile water absorbing solution separated from the growth medium, if either the bacteria or cobalamin are deleted from the experiment. The form of the volatilized cadmium species is presently unknown. In model abiotic experiments, it was shown that although highly reactive gaseous Me_2Cd is mainly decomposed by water to methane and hydrated CdO, sufficient Me-Cd bonds persist which can methylate $HgCl_2$ contained in the water absorption solution at ppm levels. In the bacterial Cd volatilization experiment, use of Hg^{2+} in the absorbing solution does yield Me-Hg products.

While a Me-Cd metabolite might be inferred from present evidence, detailed examination of the relative amounts of cadmium and "methylator" volatilized into the absorption solution compartment suggests that these are more likely coincident processes, and that there may be a significant abiotic reaction also responsible for the substantial excess of methylator over Cd produced. The work specifically concerned with the bacterial volatilization of cadmium is near completion and a preliminary manuscript has been written [14]. The work concerned with the production of "methylator", by either bacterial and/or abiotic pathways, is continuing with special emphasis on the general methylating capability of the volatile species towards a number of heavy metal ions [2,7]

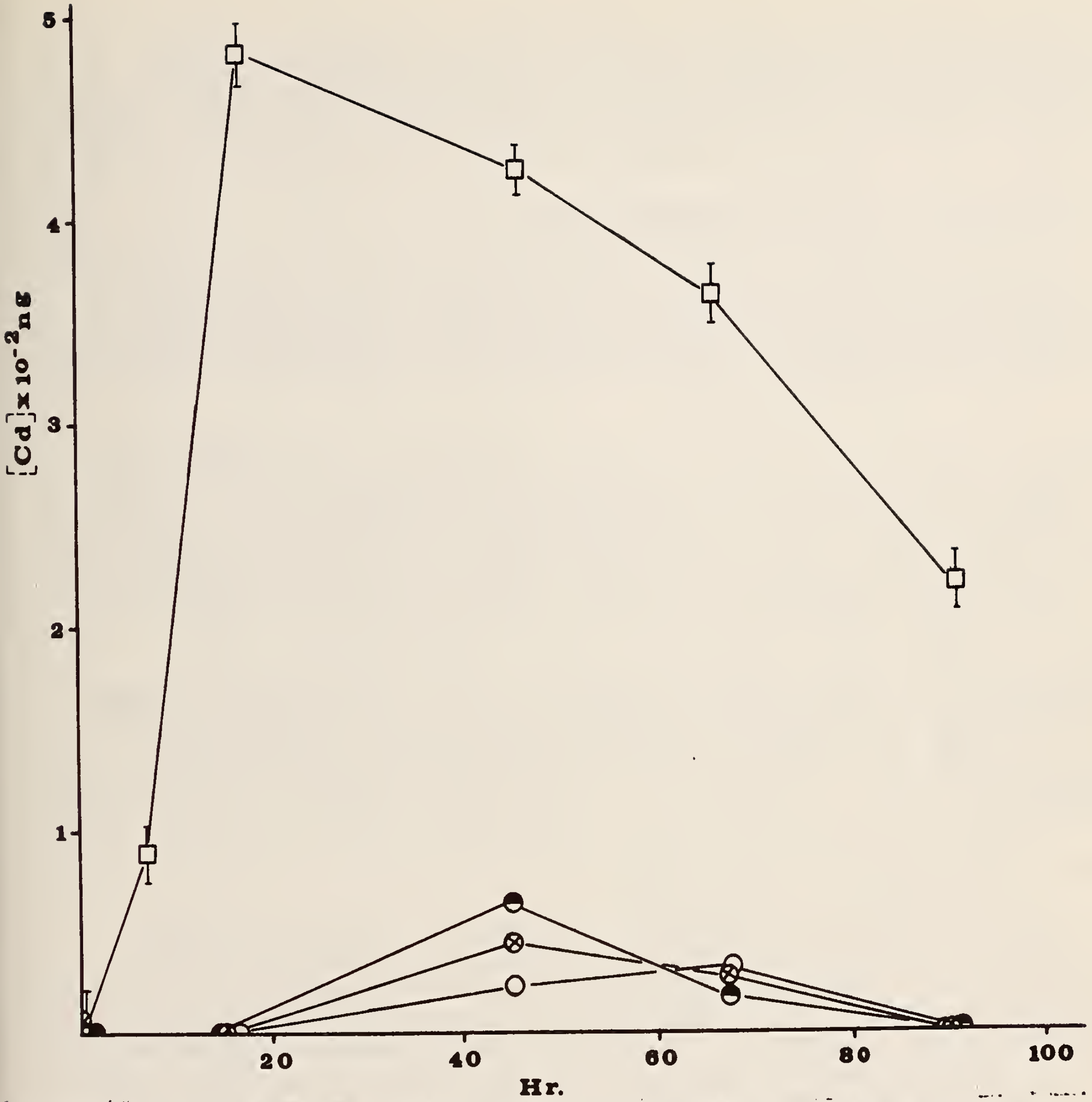


Figure 41.3.1 Cadmium volatilization by Pseudomonas sp(Ps)grown on Nelson's medium(N)doped with $5ppmCdCl_2$(Cd) is demonstrated by accumulation of transported Cd material in a separate water absorbing solution as a function of time. Compared against positive controls, the process is stimulated by presence of 2.5ppm cyanocobalamin(B_{12})curv □, whereas the system Ps+N+Cd (curve ●) alone shows little Cd transport. Additional controls testing for abiotic Cd volatilization in N+Cd+B_{12} only (⊗),or for adventitious Cd contamination with Ps+N+B_{12} (○), indicate that only the B_{12}-stimulated process is significant. The error bars depicted in the top curve apply to all four curves shown, and indicate the average deviation (± 4%) between two completely independent runs for the four-system sets described. The fall-off of Cd concentration in the absorbing solution after one day reflects a maximum growth/volatilization by the microorganism, combined with the known "plating out" of trace aqueous Cd species on glass container walls.

commonly found in sediment or sewage sludge sites. Since cobalamins are common biproducts in such sludge matrices, expected results from this line of work can yield important information regarding the potential volatilization of a number of metals well known to accumulate in such environments [5,8].

41.4 Abiotic Metal Transformations

Two other important factors responsible for the conversion of heavy metals into organometals are ligand interactions and photochemical processes. An initial effort has been made to evaluate the potential importance of these factors in bringing about metal transformations.

Examples have now appeared in the literature which show the occurrence of metal transformations in aqueous solution [8] including a wide range of transmethylation reactions between heavy metal ions [7]. On the one hand, the known cellular metabolite, methylcobalamin, has been shown to transfer with ease its methyl group to mercuric ion in aqueous solution to form the highly neurotoxic methylmercury ion [17]. In another study [18]. Jernelöv, *et al.*, have implicated anthropogenic alkyllead discharges in the formation of high methylmercury concentrations in St. Clair River sediments. Hence we have an example of methylation also occurring environmentally in apparently a straightforward metathetical reaction.

41.4a Photochemical Reactions

Work has also been advanced in the area of photochemistry. For example, a methylchromium bond has been formed in the photolysis of tertiary-butoxy radicals and chromium(II) in aqueous solution [19]. It was also found that in the presence of acetate ion or acetic acid in aqueous solution, Hg^{2+} was photolyzed in sunlight to form a methylmercury bond [20]. We have examined this latter reaction and similar ones [7]. These last reactions are consistent with early findings [21] that $(RCO_2)_2Hg$ compounds decompose in protic organic solvents under ultraviolet irradiation to yield alkyl-mercurials, RHg(OCOR).

A survey of the photolysis of acetate ion in the presence of other metal ions has also been initiated. Among other metals, thallium was selected for initial study because of the recent demonstration of its bacterial utilization and transport [22]. Thallium(I) shows evidence of involvement in a photolytic process similar to that seen for Hg(II). Thus, when thallium(I) acetate is irradiated a decrease in acetate concentration occurs; however, if a solution of sodium acetate is similarly irradiated, no diminution of acetate concentration is observed over the same period of time. Also, as with the case for Hg, continued irradiation of Tl(I) acetate finally produces free metal, along with gaseous products, including methane which might result from intermediate methylthallium(I) formation.

Two important factors emerge from these results: (1) presence of a metal cation capable of appropriate (possibly bidentate) coordination of the acetate moiety may be necessary for effective photoalkylation to occur; and (2) possible formation of a transient methylthallium(I) species, similar to those reaction intermediates reported for Pd(II) and Pt(II) forms but rapidly decomposes to observed products [7].

41.4b <u>Mercury</u>

In order to investigate the abiotic methylation of Hg^{2+} in water, the effect of ligands on reaction rate was studied. It had been previously determined that Me_3Sn^+ undergoes loss of one methyl group to quantitatively form $MeHg^+$ from aquo-Hg^{2+} as shown by equation (1) [2,7].

A major portion of the basic kinetic data required for assessing the influence of key environmental parameters of rates of transmethylation between organotin species and Hg(II) species has been completed [15]. Present results show that, both specific ligand (*e.g.*, Cl^- but not NO_3^- or ClO_4^-) and total ionic strength effects dominate the bimolecular rate law describing the reaction

$$Me_3Sn^+ + Hg^{2+} \xrightarrow{k_2} Me_2Sn^{2+} + MeHg^+ \qquad (1)$$

and that the earlier demonstrated [7] low activation energy for the transmethylation (14 Kcal) results from reaction of dissimilarly charged metal species in the transition state (Figure 41.4.1). These results are also consistent with the maximum rate for Me transfer observed at chloride ion concentrations yielding maximum formation of $HgCl_3^-$, as calculated from available formation constant data (Figure 41.4.2). The importance of other solvents on this model reaction was also evaluated. Inasmuch as available literature does not usually consider pure water as reaction medium, an understanding of relative contributions of various solvent parameters is necessary for developing a mechanistic picture for the aqueous model reaction and its extension to other metal cases.

Basically, the rate of the bimolecular process above (k_2) depends mainly on the mole fraction of water available in any miscible organic solvent. Indeed, without water present, no reaction is observed, suggesting a critical involvement of

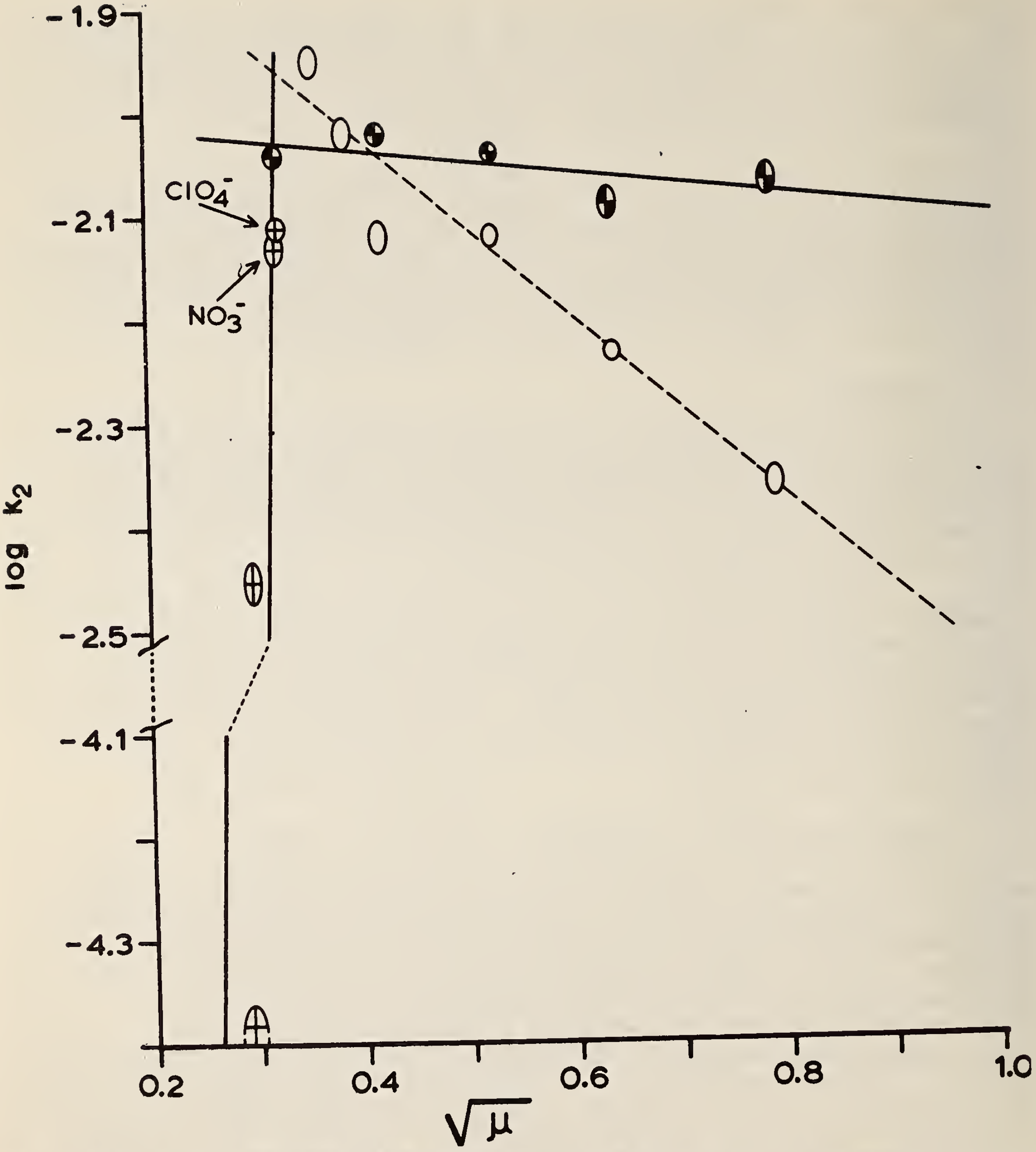


Figure41.4.1 The rate of methylation of mercuric ion by trimethyltin ion in water (expressed as log k_2) is compared at various total ionic strengths (μ) and with specific gegenions (0=Cl^- ; ◑=ClO_4^-).At nearly constant low μ ($\sqrt{\mu}\sim 0.3$) the methylation rate is dominated by salinity (eg.◑=Cl^-) and substitution of supporting gegenions such as NO_3^- ,ClO_4^- show no significant effect on this rate. Increasing ionic strength with an "inert" gegenion such as ClO_4^-(◑) reduces the rate of transmethylation, but not as severely as with increasing Cl^- (0). The negative slopes seen for $\sqrt{\mu}>0.4$ indicate that molecular species of dissimilar charge are involved in the transition state.

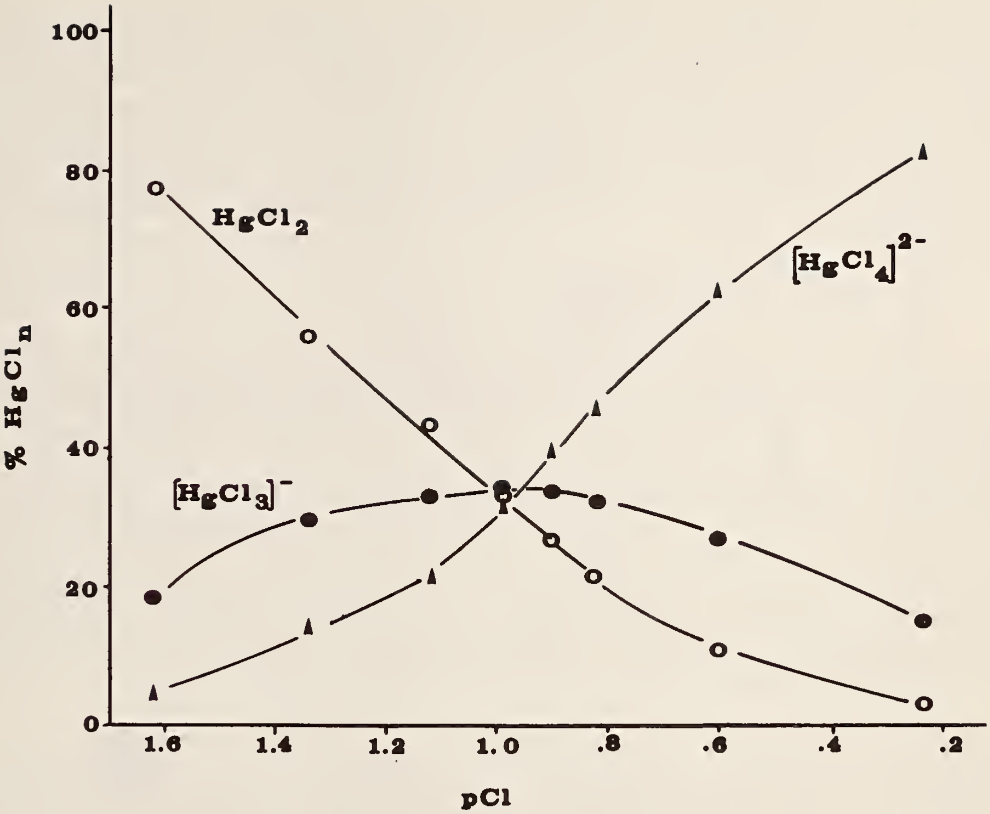


Figure 41.4.2 At the chloride ion concentrations (pCl) shown, the above mercury species are expected to occur. Although fourteen chloro- or hydroxychloro-mercury complexes can exist and their relative abundances are determined by the modified computer program, the three chloro-Hg species shown represent over 99% of total mercury present. No chloro-hydroxy- or hydroxy-mercury species at any significant concentration are indicated in the conditions employed by the present study.

water in the ionic transition state. This aspect is now under study by use of the kinetic isotope effect of trace amounts of D_2O versus H_2O in an "inert diluent" organic solvent. The ultimate goal of the present work relates to providing a model case for understanding the factors influencing transformations of known organometallic metabolites as these are transported and are transformed by passage across lipid-water interfaces.

41.4c Arsenic and Antimony

The chemical changes which facilitate the movement of arsenic and antimony from one subsystem of the biosphere to another were investigated. One of the more important processes in arsenic mobilization has been shown to be the reduction and methylation of inorganic arsenic compounds by microorganisms to produce trimethyl- and dimethylarsine [23,24,25]. At this time, it has not been demonstrated that methylstibines are metabolites of microorganisms acting on inorganic antimony compounds, but the extensive similarity of the chemistry of arsenic and antimony gives reason to believe the antimony can be biologically methylated.

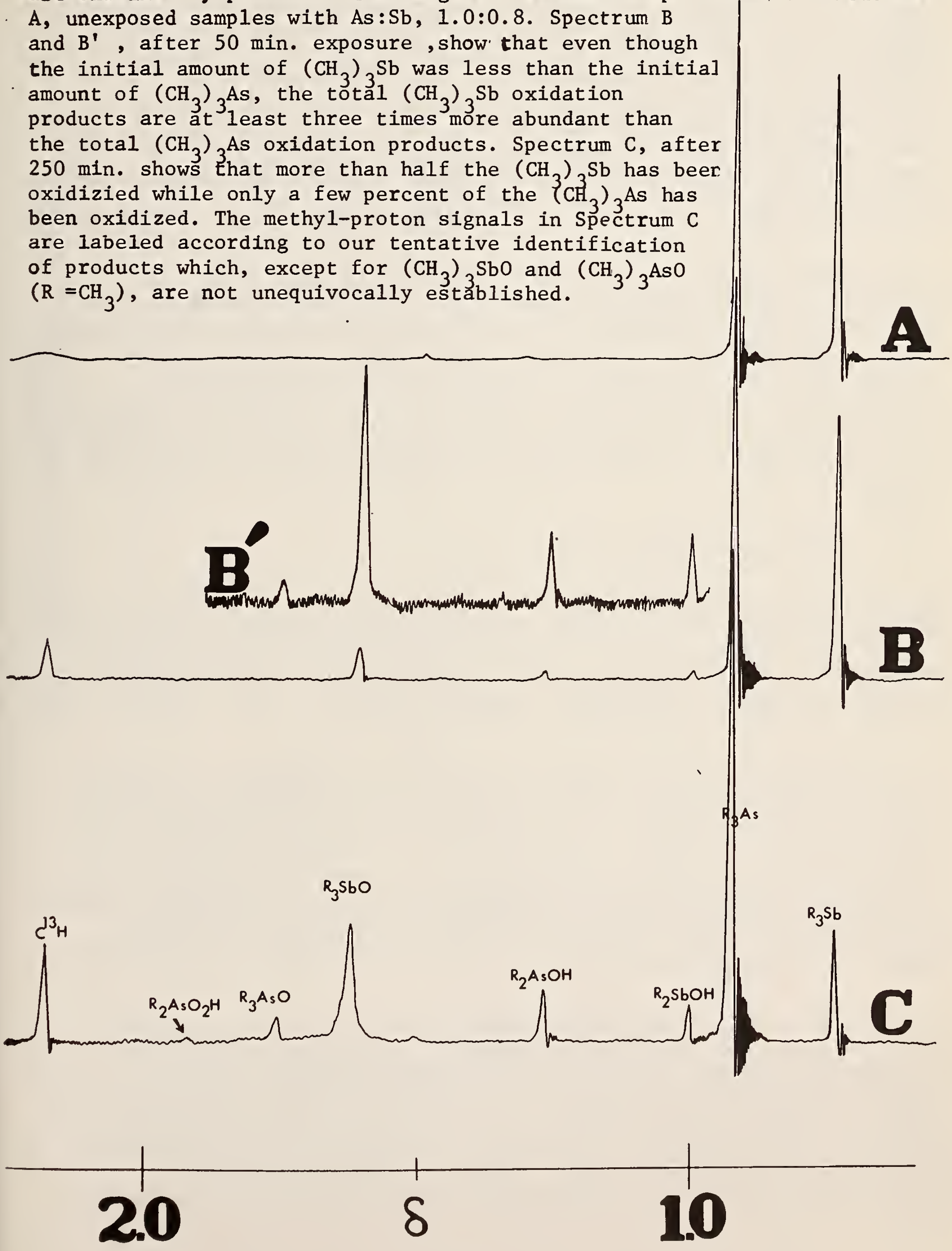
Methyl-arsines and stibines are subject to a number of reactions such as oxidation, quaternization and complex formation which could facilitate or inhibit their dispersal in the environment as well as mobility within organisms. Limited quantitative information, however, has been available to aid in assessing such redistribution possibilities. Our current efforts were devoted to establishing such a chemical data base.

Two studies on this topic have now been completed: Part I, "Quaternization of trimethylarsine and trimethylstibine"[9] and Part II, "Oxidation of Trimethylarsine and Trimethylstibine" [11]. In Part I, it was shown that the reactions of Me_3As and Me_3Sb with a variety of alkyl halides in methanol and in acetonitrile followed second-order kinetics and for that and other evidence, appeared to be a S_N2 type reaction. Twelve reactions were studied quantitatively and their reaction rates allowed the following order of nucleophilic reactivity to be established:

$$Me_3As > \text{pyridine} > Me_3Sb.$$

In Part II, this difficult problem of obtaining qualitative and semi-quantitative data on the reaction of Me_3As and Me_3Sb with molecular (atmospheric) oxygen in methanol solution and in the gas phase was examined. Figure 41.4.3] shows the qualitative observations made, using proton nuclear magnetic resonance spectroscopy (PMR), when

Figure 41.4.3 - Competitive oxidation of trimethylstibine and trimethylarsine are examined by proton nuclear magnetic resonance spectrometry. Spectrum A, unexposed samples with As:Sb, 1.0:0.8. Spectrum B and B' , after 50 min. exposure ,show that even though the initial amount of $(CH_3)_3Sb$ was less than the initial amount of $(CH_3)_3As$, the total $(CH_3)_3Sb$ oxidation products are at least three times more abundant than the total $(CH_3)_3As$ oxidation products. Spectrum C, after 250 min. shows that more than half the $(CH_3)_3Sb$ has been oxidizied while only a few percent of the $(CH_3)_3As$ has been oxidized. The methyl-proton signals in Spectrum C are labeled according to our tentative identification of products which, except for $(CH_3)_3SbO$ and $(CH_3)_3AsO$ ($R = CH_3$), are not unequivocally established.



Me_3Sb in methanol solution was allowed to react with infusing atmospheric oxygen. The principle product was trimethylstibine oxide (~80% yield) with about 20% of the antimony being accounted for as insoluble (unobserved by PMR) dimethylstibinic acid. A transient signal in the PMR spectra was due to an intermediate in the formation of the stibinic acid. Qualitatively, the reaction of Me_3As is very similar except that dimethylarsine analog (cacodylic acid) is stable. Semi-quantitative rate constants for these oxidations were deduced assuming that the reactions are first order in O_2 and Me_3As or Me_3Sb.

In general, Me_3As reacts quite slowly and can move long distances in air or oxygenated water without change, whereas Me_3Sb reacts very rapidly with O_2 in both the gas and liquid phases. We generally conclude that while volatile metabolic trimethylarsine can be expected to survive atmospheric oxidation for substantial periods of time, similar transport potential for Me_3Sb is not likely, and it is presumed that any microbial process involving methylation of Sb will not result in its volatilization as with As and some other toxic heavy metals.

41.4d Organotin Compounds

The study of specific organotin molecules released from antifouling formulations (joint NBS-NSRDL Project) has focused on two primary approaches: (1) molecular characterization of organotin species leached into aquatic environments and (2) a study of their subsequent modification at trace (micro- or nanogram) levels in natural environments.

In preliminary studies employing usual AA graphite furnace and GC parameters [12,13] no significant curvature or non-linearity was evident for calibration of volatile methyltin species from water solutions in the 1-5 ng range. A significantly different sensitivity or response was obtained for various inorganic tin solutions in the 1-5 ng range which appeared to follow expected ease of atomization based on the oxidation state or facile thermal cleavage of organotin bonds [13] (Figure 41.4.4).

Extension of this approach to speciation of several other trace organotins in aqueous samples is partially attained, but highly dependent on partition coefficients of the original analyte or a modified volatile derivative. A number of unresolved factors are also involved, including variable atomization efficiencies of aquated tin species and influence of container materials on the stability of calibration solutions containing trace quantities of organotins.

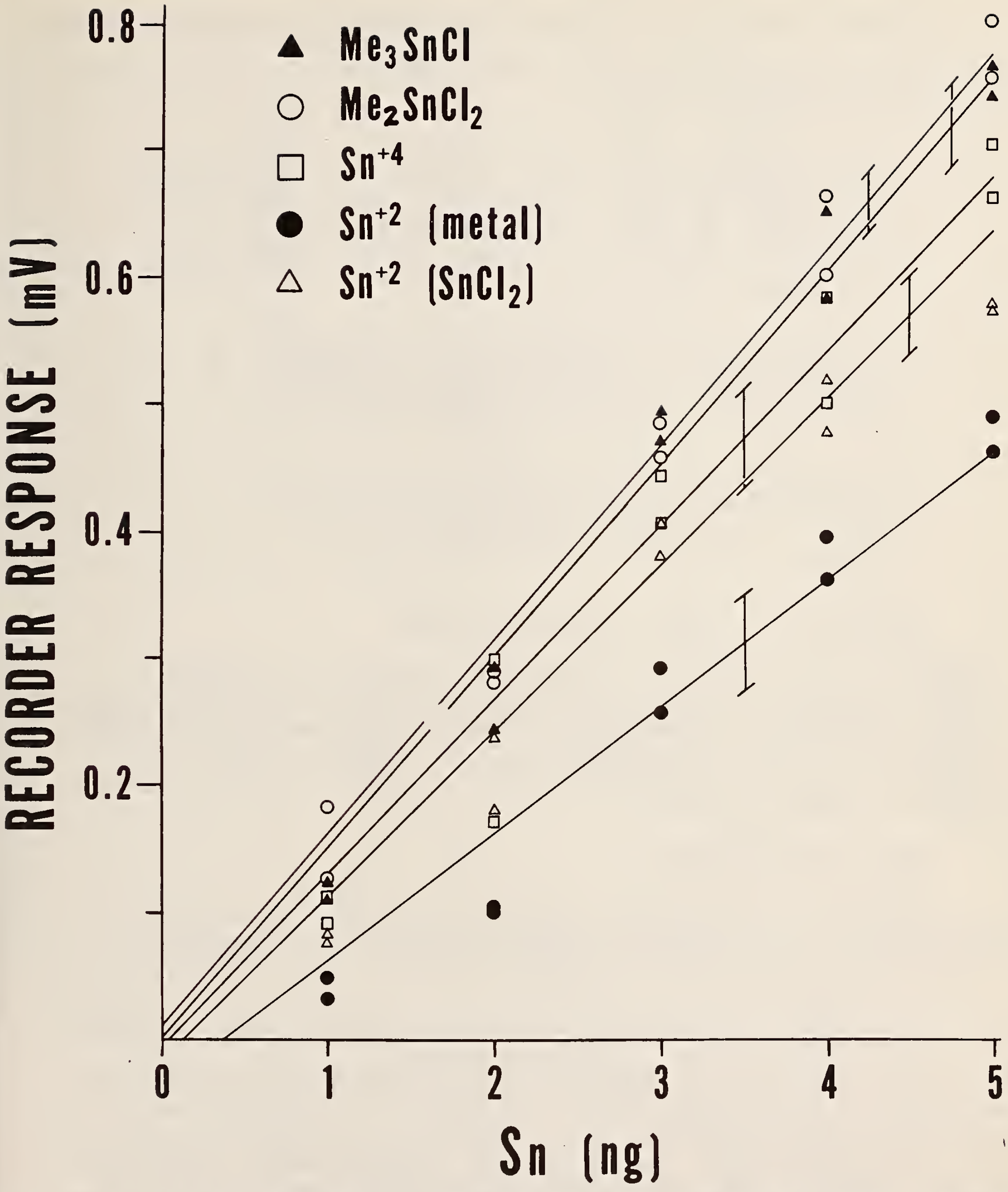


Figure 41.4.4 AA calibration curves of five tin compounds. Greater atomization efficiency (response) is indicated for Sn (IV) species as opposed to Sn (II) ions.

41.5 Electrochemistry of Trace Organometals in Aqueous Media

A collaborative effort in this topic area was recently begun for the following reasons:

a) Basic mechanism and rate data are required for elucidation of many chemical or biological steps which involve redox of metal sites bound to organic liquids; toxic methylarsenicals provide an important example as is illustrated in Figure 41.5.1.

b) Potential for developing an independent electroanalytic chemistry for certain organometallic species of environmental concern, *e.g.,* methylmercury ion.

c) Evaluation of additional certification methods required for development of an SRM for trace (ppb) methylmercury in water.

41.5a Progress to Date: Methylmercury

In collaboration with Dr. Richard M. Durst (310.05), a preliminary survey of the electrochemistry of methylmercury ion with a member of gegenions has been initiated employing principally cyclic voltammetry. Prof. John E. Doody (*cf.* Section 41.7 is also actively collaborating in the program during the summer of 1976.

41.5b Other Organometals

Electrochemistry of several methylarsenicals and organotin compounds will be surveyed utilizing cyclic voltammetry, the model compounds have now been synthesized and purified.

41.6 Workshop on Microbial Transformations of Heavy Metals

A workshop on Microbial Transformations of Heavy Metals was organized and conducted at NBS on May 10-11, 1976. The objective of this Workshop was primarily to provide a better means of communication among workers in this area than had hitherto been possible at the International Conference held over the past several years. Other objectives would be to permit a better understanding of the progress made in these areas, and to envision areas when significant gaps were missing in understanding the overall significance of heavy metals transformations by microorganisms in the environment.

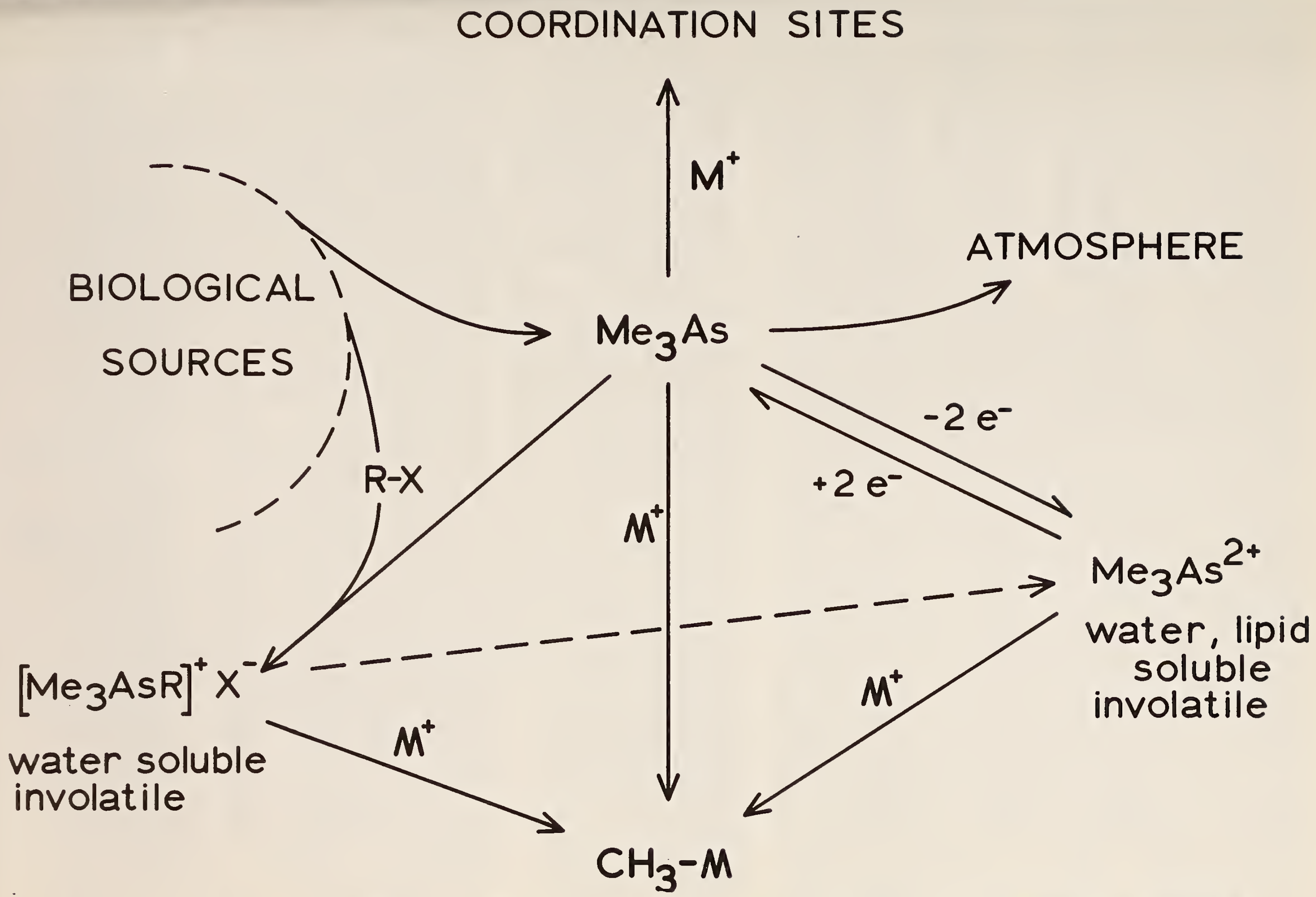


Figure 41.5.1 Example of potential transport chemistry available for toxic organoarsenials, showing involvement of redox chemistry as an integral process.

There were about 32 people in attendance including 18 invited participants. The three main areas of discussion were: (1) techniques for detection and speciation of volatile heavy metals, (2) bacterial transformation of heavy metals and (3) extrachromosome elements as determination in metal tolerance and metal transformations of bacteria.

41.7 NBS-NSF Faculty Participation Research Program

The NBS was awarded funds by NSF sufficient to support two senior academicians for the summer of 1976.

41.7a Objective and Mechanism

The NSF program of Faculty Research Participation provides opportunities for academic faculty to participate in industrial research activities. The purpose of providing this experience in research on problems on national interest and concern is to encourage and assist teachers in re-evaluating the relevance of their course materials to the needs of students being prepared for applying the results of their education in the national society.

In the program, a research facility proposes to the National Science Foundation to offer selected academic faculty opportunities to participate for ten weeks during the summer in the ongoing research activities of the facility. The projects available during the summer are announced to the academic community in the preceding spring. Interested faculty then apply for participation directly to the facility. The participants in a project are selected by the research facility from the applications submitted to it.

The research opportunities or problems are specified by the facility. They are to be immediately relevant to the interests and concerns for which the facility is maintained, amenable to a valid and effective application of scientific method, and appropriate to the conditions of support provided by the Faculty Research Participation Program, and to its goals. The project plan provides for the faculty to work as resident participants in ongoing research activities of the facility.

41.7b NBS Summer Participation Projects

Three separate but parallel topic areas were made available for study by senior workers under the auspices of the NSF Faculty Research Participation Program. These represented the main disciplinary concerns which provide impetus to the overall NBS project, and which from appropriate new academic experience can play an immediate role in advancing our work.

Conventional laboratory facilities and instrumentation were already available for successful faculty participants, and a number of special manipulative and detection systems for the biotransformation studies are also available.

The topic areas listed reflect distinct academic experience and interest. They overlap to a substantial degree, depending on individual persuasion and availability, but are set out separately in order to better define the range of interest within the NBS project on Environmental Metals Transformations:

Abiotic Transmethylation Reactions of Heavy Metals in Aquatic Systems - represents our continuing interest in extending the descriptive organometallic chemistry of aquated heavy metal ions in water and related protic media.

Biotransformations of Heavy Metals in the Environment - involves the ongoing interdivision program which combines NBS expertise in microbial corrosion and inorganic chemistry. The work is directed to active field studies providing bacterial isolates and representative biological matrices for laboratory investigation of metal transport and speciation.

Speciation of Trace Organometallics in the Environment - draws on NBS interests and expertise in advancing analytical and characterization methodology. While not viewed principally as an analytical effort, academic interest in those areas concerned with trace determinations of metal-containing molecules derived from, or within, biological matrices will offer considerable support to the overall project.

41.7c Selection NBS-NSF Faculty Participants

Following announcement of the joint NBS-NSF project, a substantial number of applications were received. Among 14 eligible applicants, two were selected: Professor John E. Doody, F.S.C. Christian Brothers College, Memphis, Tenn.--to conduct research on speciation and electroanalytical investigation on toxic organometallic compounds in aqueous media. Professor J. M. Bellama, University of Maryland, College Park, MD--to study the possible transfer of alkyl (methyl) groups from methyl silicones, and model trimethylsilyl compounds similar to such industrial materials, to other metal species in order to establish potential for environmental hazards.

Both recipients of the NBS-NSF award have been appointed as NBS Guest Workers in order to provide continuity for completing publication of their research following the 10-week contact period.

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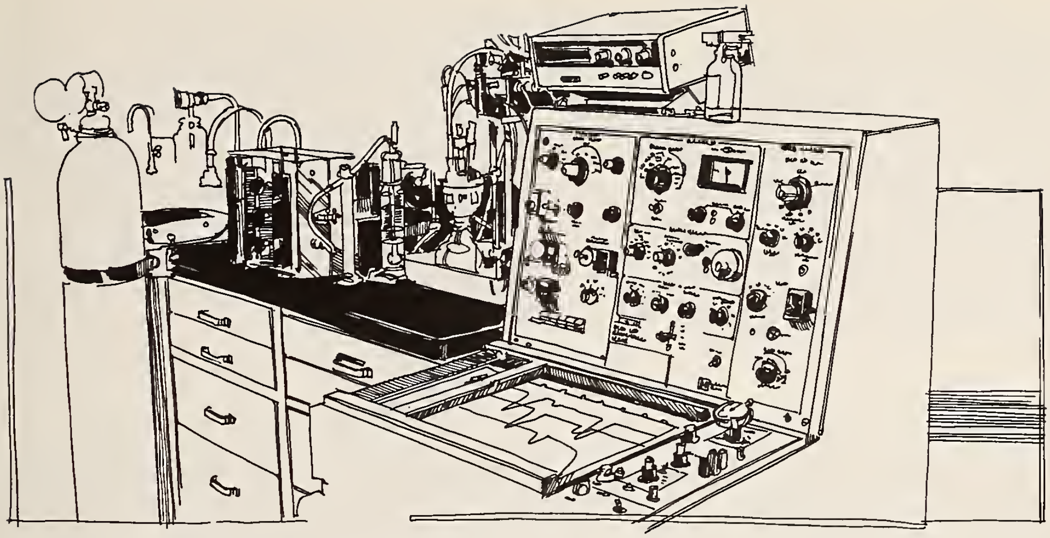


42. Heavy Metal Speciation

Project Leader: Richard A. Durst, Analytical Chemistry Division

Approach

Heavy metal elements such as cadmium, lead and copper undergo extensive chemical and biochemical modifications when released into the environment. In natural waters, the metals may exist simultaneously in a variety of forms including free ions, complexes, particulates, and organometallic compounds. Since it has been demonstrated that there is a close relationship between toxicity and speciation, the determination of the forms of the metals is at least as important as the total concentration. Because the analytical techniques conventionally used for the measurement of trace heavy metals require sample pretreatment operations which destroy the various forms present, few data are available on the very important question of heavy metal speciation in natural waters.

Electroanalytical techniques can provide a unique and convenient means for performing speciation analyses in situ without the need for preconcentration or chemical pretreatment, by virtue of their high analytical sensitivity, selectivity, and sensitivity to complex formation and oxidation states of the metal ions. Accordingly, the techniques of polarography, anodic stripping voltammetry, and ion-selective electrode potentiometry will be applied to the elucidation of copper, cadmium, and lead speciation in various natural waters. This work will progress along several lines of research including:

sampling and sample storage, evaluation of techniques, gross sample characterization, speciation by chemical and instrumental differentiation, equilibria and kinetics studies, effects of ambient environmental conditions, intercomparison of natural waters, and bioreactor studies of the distribution of heavy metals between the solution, sediment, and biota. The development of the techniques and studies of the type noted above will help provide the data necessary to set realistic toxicity standards and the means to monitor the natural waters for specified toxic species.

Progress

The evaluation of voltammetric techniques has been initiated using the P.A.R. Model 170 Electrochemistry System to provide the various functional modes required for this study. This system, which is new, has been set up to perform experiments in polarography and stripping voltammetry, using a classical dropping mercury electrode (DME), a rotating glassy carbon electrode (RGCE), or a hanging mercury drop electrode (HMDE). As part of the overall system, a special gas mixing manifold has been constructed in this laboratory to provide precisely blended carbon dioxide-nitrogen mixtures for the dual purpose of deaeration and pH control of the sample. By means of flow meters and differential flow regulators, it is possible to accurately control the amount of CO_2 in N_2 at any value between 0 and 100 percent and the flow rate up to 200 cm^3/min.

Although some of the initial testing was performed using the DME, and this electrode may be used in future work with the differential pulse mode of operation, this mode is not functioning properly on the present instrument and further work with differential pulse polarography must await repairs to the instrument. The most recent work has involved optimizing the operational parameters for performing anodic stripping voltammetry (ASV) with the RGCE and in situ plating of a thin film of mercury on the glassy carbon. Although ASV can be performed using differential pulse stripping for maximum sensitivity, the present evaluation work has concentrated on conventional linear d.c. scan stripping.

Using millimolar sodium carbonate and millimolar sodium acetate supporting electrolytes (which were purified by continuous controlled-potential electrolysis), it has been possible to determine 0.5 ppb of copper, cadmium, and lead in synthetic solutions. These levels are consistent with those anticipated in the natural samples to be studied in the future. The peaks obtained for these three elements are completely resolved by this technique (see Figure 42.1). Although there is no problem in terms of sensitivity and selectivity with the synthetic solutions under study, matrix effects in the natural samples may pose problems in terms of interferences and long-term stability of the samples.

Most of the recent work has involved evaluation of the precision of the ASV method when using two different types of working electrode: the thin mercury film glassy carbon electrode (TMFGCE) plated in situ and the hanging mercury drop electrode (HMDE). Although the TMFGCE has the advantages of higher sensitivity and resolution, it suffers from two serious disadvantages. First, plating in situ requires spiking the sample solution to about 10^{-5} M in mercuric ion which would upset trace metal equilibria in an actual environmental sample, and also poison heavy metal ion-selective electrodes used in simultaneous measurements. Second, the presence of the glassy carbon substrate requires multiple plate/strip cycles in order to obtain reproducible results.

This is a reflection of variations in the thin film caused by incomplete stripping of the mercury film between scans.

For the work planned, it appears that the TMFGCE is not suitable and, in the absence of the differential pulse mode, only d.c. ASV with the HMDE will be applicable, although its limited sensitivity may not be sufficient for the lowest heavy metal concentrations encountered.

During this period, attention has been focussed on two heavy metals: cadmium and mercury. Calibration curves developed for the cadmium ion-selective electrode have demonstrated its utility to less than 100 ppb of cadmium. In the 10-100 ppb range, the electrode response is highly dependent on the electrode conditioning procedure, which is currently being optimized.

Because of the enhanced toxicity of mercury as organomercurials, especially methylmercury, electrochemical methods were applied to the quantitation of the compound. Initially, cyclic voltammetry (CV) was used to observe the overall redox behavior. During this study, a previously unreported reduction (or adsorption) peak was observed during the anodic cycle of the scan (see Figure 42.2). This observation, along with other unreported fine structure in the cyclic voltammograms, may provide new insights into the mechanisms of mercury transformations.

Using a P.A.R. Model 174 polarograph in the differential pulse mode, the first reduction wave of methylmercury was quantified by a standard addition procedure. Linear response was observed over the concentration range from 60 to 900 ppb. It is anticipated that the detection limit can be further reduced to 10 ppb or less.

In preparation for studies of complexation by natural substances, two commercial samples of humic acid were obtained. Saturated solutions were prepared and the resulting mixtures characterized by sedimentation. One sample separated into two layers (a light-brown colloidal solution phase and a dark-brown sediment) in one day, while the other sample sedimented into several layers after two days and into the two final layers (as above) after more than three days. From this simple experiment, it is clear that considerable differences exist in humic acids depending on their source and method of preparation. It was also found that for both of these samples the soluble (fulvic acid) and colloidal fraction represented a concentration of 0.15 ± .02 percent by weight.

Future studies of cadmium-fulvic acid complexation will be performed under controlled conditions in which the alkalinity and pH are fixed by $NaHCO_3$ solutions equilibrated with CO_2/N_2 mixtures in order to first measure hydroxide and carbonate complexation. The interactions of cadmium and fulvic acid will then be monitored by means of the ion-selective electrode and differential pulse polarography.

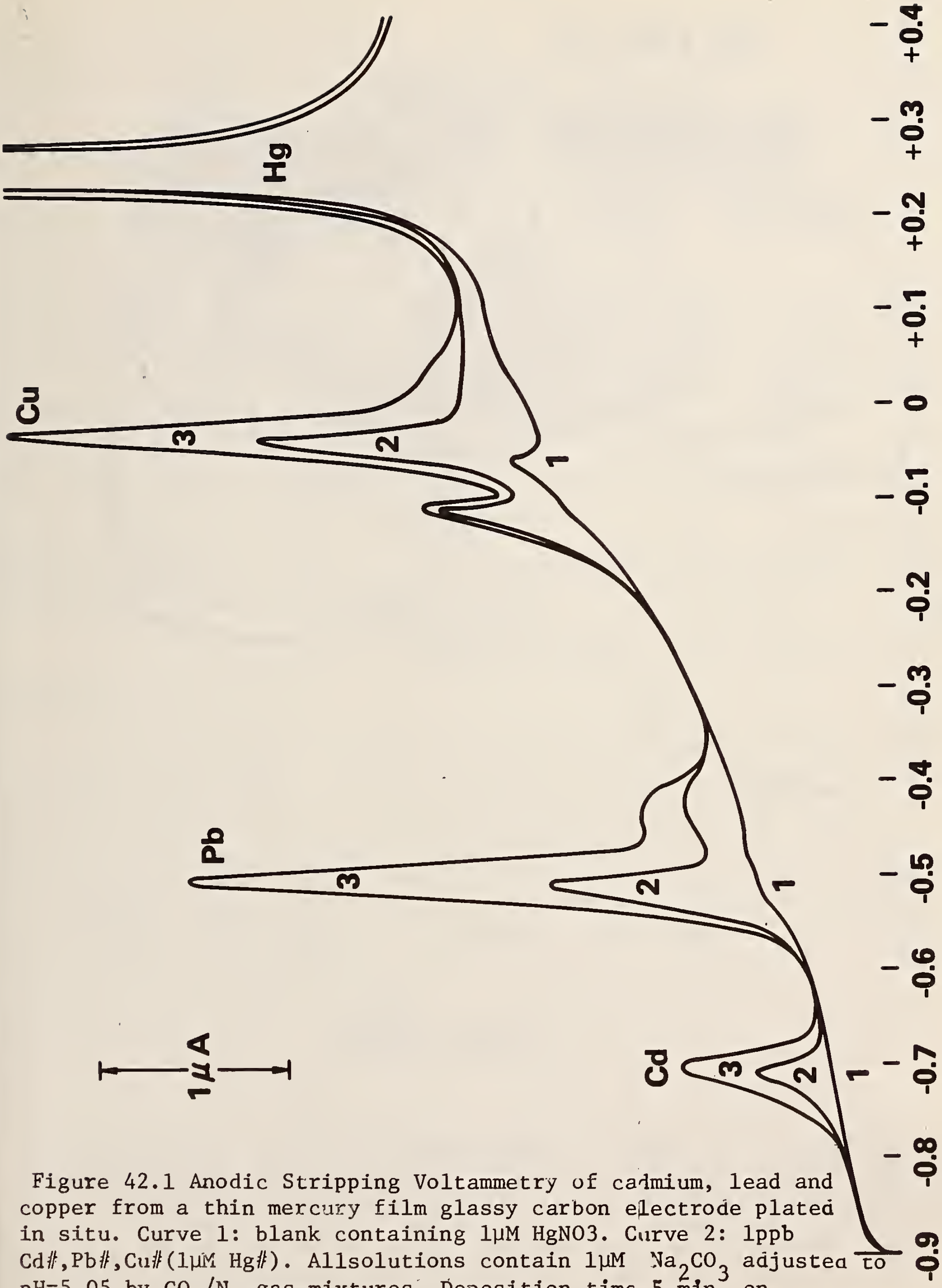


Figure 42.1 Anodic Stripping Voltammetry of cadmium, lead and copper from a thin mercury film glassy carbon electrode plated in situ. Curve 1: blank containing 1µM HgNO3. Curve 2: 1ppb Cd#,Pb#,Cu#(1µM Hg#). Allsolutions contain 1µM Na_2CO_3 adjusted to pH=5.05 by CO_2/N_2 gas mixtures. Deposition time 5 min. on rotating GCE (650 rpm). Stripping scan rate: 50 mV/s.

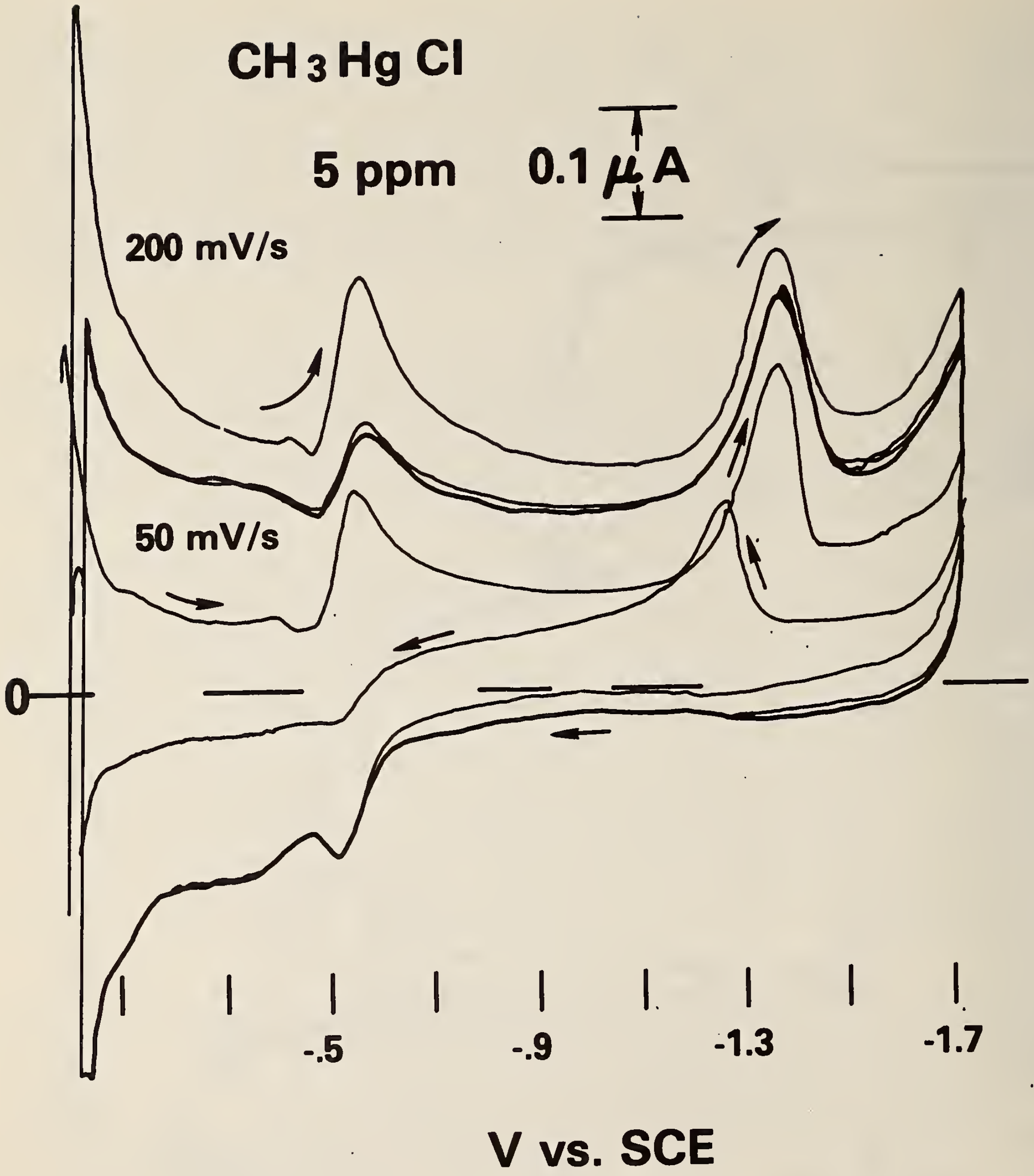
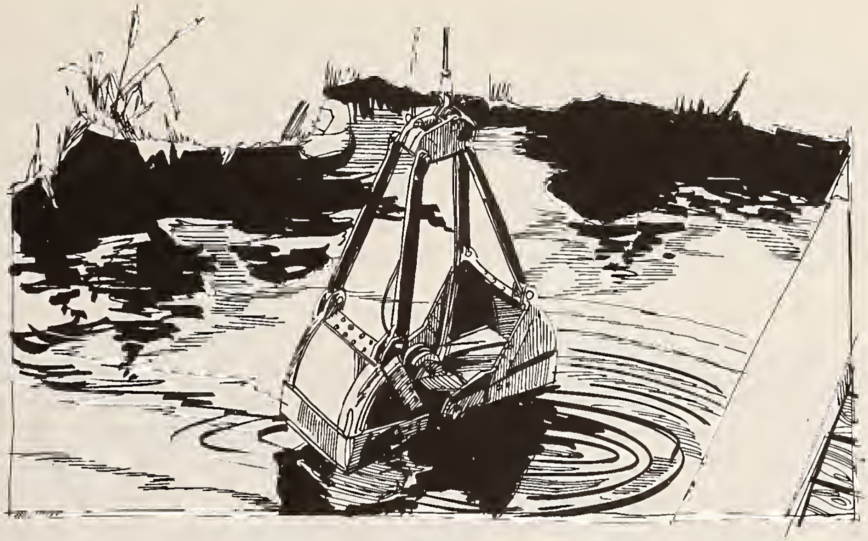


Figure 42.2 Cyclic Voltammetry of methylmercury chloride. Cathodic scan shows two reduction peaks at -0.6 and -1.4 V. Anodic scan at 50mV/s shows an anomalous reduction peak at -1.3 V which disappears at 200mV/s.



43. Development of Reference Materials for Sediment Analysis

Project Leader: John K. Taylor, Analytical Chemistry Division
Other Personnel: Harry Rook, E. R. Deardorff, M. Darr, and W. P. Schmidt

Objective

The objective of this project is to develop and characterize reference standards for the chemical analysis of sediment materials in the beds of rivers, lakes, and harbors. The reliability of the chemical analysis of sediments from bodies of water, required for environmental impact studies for example, is unknown. Discordant results are partly due to sampling problems as well as to analytical uncertainties. Concern about this situation by many analysts and especially by EPA, has prompted the latter to sponsor a project at NBS to provide reference standards. The availability of such standards will make possible the evaluation of methods used for the analysis of key substances, and stimulate the development of new techniques where existing ones are inadequate. Above all, the standards should verify the accuracy of analytical values obtained for environmental impact studies used for the basis of environmental decisions and minimize controversy presently based on discrepancies in analytical data. While initially intended to help EPA in its regulatory problems, the materials are expected to ultimately appear as Standard Reference Materials, for use both as quality control purposes and as general reference materials for analytical research and development.

Approach

A series of sediments will be obtained from typical locations--rivers, lakes, harbors--homogenized and their stability studied under storage conditions. Materials of most suitable composition will be selected, in consultation with EPA and analyzed by state-of-the-art procedures for such components as toxic metals, nutrients, and a variety of organic compounds.

Progress

Work during Fiscal Year 1974, concerned with examination of candidate sediments, provided the basis for selection of the Indiana Harbor Canal as the site for collection of the large amount of material for use as reference standard. A large quantity of sediment (approximately 2500 lb) was collected by means of a clam-shell dredge. A preliminary screening was done to remove foreign objects.

The screened material was freeze-dried under contract by a commercial processor prior to delivery to NBS. The material was then radiation sterilized as a precautionary measure.

Preliminary studies indicated that homogeneity would be facilitated by sieving through a 80-mesh screen. This was done and the material so treated was accepted as the sample. This was extensively mixed in a V-blender before bottling. The material was then packaged to obtain 5000 bottles, each containing 80 g of sediment.

Initial homogeneity studies were made on the blended material by neutron activation analysis and by measurement of the chemical oxygen demand (dichromate method) but the major investigation was done after bottling. A statistical sampling of 30 bottles from the lot was used for measurement of the following parameters: chemical oxygen demand; loss on ignition; total phosphorous; Kjeldahl nitrogen; heavy metals by x-ray fluorescence measurement. These measurements indicate that these and other parameters are not expected to vary more than 2 percent between bottles, making the material adequate for the intended purpose.

Certification analyses have been initiated for issuing the material as a Standard Reference Material. The analytical work is substantially complete and the material is expected to be issued as SRM #1645, River Sediment on or about January 1, 1977. The development of additional sediment reference materials, including a marine sediment, is under consideration. In the meantime, 2500 bottles of the material have been delivered to EPA for use by them in method evaluation studies.

Publications

[1]. Taylor, J.K. and Rook, H.L., Development of a Reference Material for Sediment Analysis. Publ. 208 (1975).

44. Development of Precipitation Standards

Project Leader: J. K. Taylor, Analytical Chemistry Division
Other Personnel: E. R. Deardorff, R. A. Durst, E. J. Maienthal, T. C. Rains, and E. P. Scheide

Objective

The chemical composition of atmospheric precipitation (e.g., rainwater) is an important indicator of pollution levels. The analysis of precipitation must be done on a global scale and by use of techniques which are presently not standardized. At the request of EPA, and under their sponsorship, NBS initiated a project to develop reference materials that could be used to evaluate the various methods presently in use for this purpose, and to serve as quality control materials for data collected in global monitoring programs.

Approach

Dilute solutions containing 10 commonly occurring metallic elements and 5 anions associated with them were prepared in such concentrations that, on dilution with pure water, they would simulate the full range of concentrations found in atmospheric samples. A series of 4 samples were utilized for this purpose. After initial studies of stability and compatibility of components, the samples were prepared in bulk and sealed in individual ampoules for subsequent dilution at time of use. The most accurate analytical techniques presently available were used to certify their composition and to attest the homogeneity between individual samples. In addition two "blind samples" were prepared in a similar manner for use by the World Meteorological Organization in a quality control program.

Progress

This project was completed during Fiscal Year 1976. The reference materials were prepared in concentrations such that a 50-fold dilution would produce solutions simulating the composition of natural rainwater. Four levels were prepared to cover the range found in various locations. The complexity of precipitation analysis is evident from inspection of the number of components and the concentration levels involved:

Constituent, ionic	Range, mg/l
Sulfate	1-10
Nitrate, Fluoride, Chloride	0.1-18
Ammonium, Sodium	0.1- 5
Potassium	0.1- 3
Calcium, Magnesium	0.1- 3
Zinc, Cadmium, Copper Nickel, Lead, Manganese	0.02-1

The solutions were prepared in bulk by dissolving the pure salts in water. They were sealed in 10 ml ampoules using the automatic filling equipment of the NBS Office of Standard Reference Materials. In use, the samples will be quantitatively diluted to 500 ml to prepare reference samples at the indicated concentration levels.

While the concentrations are expected to be stable for a limited time, neither their long-term stability nor the stability of the diluted solutions is presently known. Accordingly, samples from the productions lot have been retained and will be analyzed periodically to answer such questions which are important if Standard Reference Materials of this kind are considered.

Three hundred ampoules were prepared at each of three levels and five hundred were prepared at a fourth concentration level. The original bulk solutions were analyzed and statistically selected ampoules from the production lot were also measured.

Publications

[1]. Taylor, J.K., Deardorff, E.R., Durst, R.A., Maienthal, E.J., Rains, T.C. and Schiede, E.P., Simulated Precipitation Reference Materials, *NBSIR 75-958*(1975).

45. Mixed Heavy Metals in Water SRM

Project Leader: I. L. Barnes, Analytical Chemistry Division

Other Personnel: B. I. Diamondstone, E. L. Garner, J. W. Gramlich, J. R. Moody, T. J. Murphy, P. J. Paulsen, T. C. Rains, and H. L. Rook

Objective

To determine stability of mixed heavy metals in acidified water and to investigate methods for certification of at least ten elements at the ng/g concentration level.

Approach

A solution of ten mixed heavy metals in 0.5N nitric acid solution was to be analyzed during the first week after preparation and at 6 and 16 week intervals. The concentration of these elements was selected to be at the upper limit of the proposed EPA standard. The techniques to be used were neutron activation analysis, atomic absorption spectrophotometry, isotope dilution mass spectrometry, spark source isotope dilution mass spectrometry and spectrofluorimetry.

The stability of the trace elements in the solution were to be studied in Teflon FEP, polyethylene, and quartz containers.

Progress

Preparation of Solution: The Teflon FEP, quartz, and polyethylene bottles used in this study were thoroughly cleaned by prolonged leaching with diluted nitric and hydrochloric acids. A large 24 liter polyethylene carboy was cleaned by storing (1+10) HNO_3 in the carboy for several weeks. The carboy was then emptied, rinsed, and filled with ultra pure water three times.

The elements to be incorporated into the standard were arsenic, beryllium, cadmium, chromium, copper, mercury, manganese, lead, selenium, and zinc. A trace quantity of gold was to be added to stabilize mercury. Standards of varying concentrations (Table 45.1) were prepared by dissolving weighted amounts of the pure element (as metal) in acid and diluting to 10 ml in a volumetric flask. An intermediate solution of As, Si, Cr, Cd, Pb, Mn, Be, Au, and Hg was prepared by adding aliquots of the standard solutions of the elements to another volumetric flask and diluting to volume. Since this was a trial solution no attempt was made to calibrate the glassware used. The 24 liter carboy was filled (by weight) with 23 liters of 0.5N nitric acid. An aliquot of the intermediate solution and separate aliquots of the Cu and Zn standards were added and the solution was stirred for 16 hours by a magnetic stirrer. The solution was then transferred to 15 one liter Teflon bottles, 9 two-hundred-fifty milliliter quartz flasks and 12 five-hundred milliliter polyethylene bottles.

Analysis of Standard: The initial analysis for all elements were taken within one week of preparation of the standard. With the exception of arsenic, the results were in fairly good agreement with the calculated concentration. Arsenic was 30 percent low and may have been lost during the preparation of the sample.

Considering the concentration of the mixed heavy metals, the agreement between techniques was good for some elements (Be, Cu, Hg, and Zn) but poor for others (Cd, Cr, Mn, and Se). It ranged from 0.5 percent for Be to 50 percent for selenium. Obviously, more work is needed before some elements could be certified in a standard.

The standard was again sampled and analyzed after 17 weeks storage in the containers. The results as reported in Table 45.1 show that no significant loss of any element occurred over this time interval. For some elements there are apparent increases in concentration when stored in Teflon but these are within analytical uncertainties.

The results of analyses after storage in Teflon, polyethylene and quartz are shown in Table 45.2. For the most elements, there was no apparent difference between the three materials. There was an apparent increase in mercury content on storage in polyethylene but further determinations are necessary to verify this. Based on these results and the fact the quartz flasks are difficult to seal, Teflon would be the preferred container material for a future standard.

Future plans call for the refinement of measurement methodology and the re-analysis of this standard at a three to six month interval to further study stability on storage. We plan to propose to the Office of Standard Reference Materials that a SRM of mixed heavy metals in water be certified but with lower copper and zinc concentrations.

TABLE 45.1 Multi-Element Water Standard Stored in Teflon FEP

Calculated Concentration μg/g		Initial Analysis μg/g		Analysis after 17 weeks μg/g	
As	0.0937	0.0603	NAA	0.0630	NAA
		0.062	AA	0.0599	AA
Au	0.0017				
Be	0.0397	0.0404	AA	0.0412	AA
		0.0406	SF	0.0409	SF
Cd	0.01365	0.0146	NAA		
		0.0146	AA	0.0149	AA
		0.0185	SS		
Cr	~0.047	0.060	NAA	0.056	NAA
		0.0498	AA	0.0471	AA
		0.053	SS		
Cu	0.8069	0.851	AA	0.849	AA
		0.814	NAA	0.849	NAA
		0.78	SS	0.848	IDMS
Hg	0.00184	0.0018	NAA		
		0.00182	AA	0.00175	AA
Mn	0.0418	0.042	NAA	0.047	NAA
		0.0391	AA	0.0455	AA
Pb	0.0469	0.0498	AA	0.0459	AA
		0.0467	IDMS	0.0465	IDMS
Se	0.01009	0.0105	NAA		
		0.0107	AA	0.0098	AA
		0.016	SS		
Zn	4.8928	4.96	NAA	5.08	NAA
		4.96	AA	5.083	AA
		5.16	SS		

Key:	AA	Atomic Absorption Spectrophotometry
	IDMS	Isotope Dilution Mass Spectrometry
	NAA	Neutron Activation Analysis
	SS	Spark Source Isotope Dilution Mass Spectrometry
	SF	Spectrofluorimetry

TABLE 45.2 Storage of Multi-Element Water Standard in Various Containers[a]

Element	Teflon		Polyethylene		Quartz	
	Initial μg/g	17 Weeks μg/g	Initial μg/g	17 Weeks μg/g	Initial μg/g	17 Weeks μg/g
As	0.062	0.0599	0.064	0.0595	0.064	0.0591
Be	0.0404	0.0412	0.0381	0.0412	0.040	0.0417
Cd	0.0146	0.0149	0.0138	0.0141		0.0146
Cr	0.0498	0.0471	0.0481	0.0473	0.0488	0.0467
Cu	0.851	0.856	0.850	0.855	0.852	0.857
Hg	0.00182	0.00175	0.00209	0.0246	0.00186	0.00183
Mn	0.0391	0.0455	0.0398	0.0459	0.0386	0.0461
Pb	0.0498	0.0459	0.0492	0.0471	0.0484	0.0476
Se	0.0107	0.00986	0.0128	0.00986	0.0112	0.00966
Zn	4.96	5.083	4.98	5.096	4.97	5.075

[a] All determinations by atomic absorption spectrophotometry.

46. Trace Hydrocarbon Analysis

Project Leaders: H. S. Hertz and S. N. Chesler
Analytical Chemistry Division

Other Personnel: S. M. Dyszel, D. P. Enagonio, B. H. Gump,
D. A. Becker, and W. E. May

Objective

To develop chromatographic and mass spectrometric separation and analysis techniques for the quantitative determination of trace levels of petroleum hydrocarbons, especially aromatic hydrocarbons. To establish meaningful analytical values for existing levels of crude oil pollution in the marine environment.

Progress

The method of analysis developed in this laboratory [1,2] involves dynamic headspace sampling for volatile hydrocarbon components of the sample followed by coupled-column liquid chromatography for the non-volatile components. These techniques require minimal sample handling, reducing the risk of sample component loss and/or sample contamination.

Volatile sample components are separated from the matrix in a closed system and concentrated on a TENAX-GC packed pre-column, free from large amounts of solvent and ready for GC/GC-MS analysis. Non-volatile compounds, such as the benzpyrenes, may be extracted from large volumes of water and concentrated on a Bondapak C18 packed pre-column for coupled-column liquid chromatographic separation and analysis.

Prior to the development of oil transfer facilities in Port Valdez and exploratory drilling in the Northeastern Gulf of Alaska, this area is presently relatively pristine, the principal economic activity being commercial fisheries. Except near natural oil seeps, hydrocarbons in the environment are expected to be present at the microgram per kilogram level and may well be non-petroleum in origin. A number of sites were selected for sampling within the Prince William Sound and the Northeastern Gulf of Alaska to reflect the various types of environments found there. Tables 46.1 and 46.2 summarize the data obtained over several seasons for sediment and water from these various sites.

Some seasonal variability in hydrocarbon content is observed in the different sites, however, no reproducible pattern is discernible. High values do not necessarily represent petroleum pollution but could be of biological origin.

Included in this report are results of a detailed GC-MS analysis of sediment from Katalla River. The gas chromatogram obtained from the sediment indicated the presence of a "petroleum hump". The total ion chromatogram (computer-generated gas chromatogram) for the sediment is presented in Figure 46.1C.[1] Figure 46.1B contains the m/e 43 mass chromatogram for the sample. (Mass chromatograms are computer-generated mass specific gas chromatograms used in locating particular compounds or classes of compounds containing an indicative m/e peak in their mass spectra.) A peak at m/e 43 is indicative of aliphatic hydrocarbons and in Figure 46.1B this mass chromatogram helps identify the homologous series which one could not have visually identified in the complex gas chromatogram.

The GC-MS analyses of the sediments from Katalla River confirm that the major constituents are all hydrocarbons. Due to the large number of aromatic hydrocarbons and to the absence of any even/odd preference in the aliphatic series, the presence of petroleum is indicated. This is an expected result since the Katalla River site is downstream from known oil seeps. One final note of interest concerns the complexity of the petroleum hump, which contains a large number of unresolved hydrocarbons. By the use of mass chromatograms some compounds can be easily resolved. An example is shown in Figure 46.1A which contains the composite mass chromatograms for m/e 142, 156, and 170, the molecular ions indicating the presence of C_1, C_2, and C_3-naphthalenes, respectively.

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[1] See last page of text for detailed information on Figure 46.1 C.

Site/Season	Total maximum hydrocarbon Content (μg/kg wet weight) Obtained by Headspace Sampling	Percent of total Hydrocarbons by Molecular Weight Region			
		Mesitylene	Naphthalene	Propylnaphthalene (or Trimethylnaphthalene)	Phenanthrene
Hinchinbrook Is.					
Summer 73	83 (1) [a]	35	29	36	
Fall 73	115 (1)	26	26	48	
Spring 74	63 ± 10 (4)	43 ± 9	26 ± 3	31 ± 10	
Fall 74	91 ± 29 (4)	25 ± 10	10 ± 2	10 ± 2	51 ± 11
Mineral Creek					
Summer 73	121	31	34	34	
Fall 73	147 ± 20 (4)	29 ± 4	28 ± 1	42 ± 4	
Spring 74	190 ± 2 (2)	32 ± 6	26 ± 2	42 ± 6	
Dayville Mud Flats					
Summer 73	254 ± 12 (3)	28 ± 2	30 ± 2	42 ± 1	
Fall 73	153 ± 23 (3)	30 ± 8	26 ± 3	44 ± 7	
Spring 74	147 ± 51 (1)	33 ± 15	26 ± 3	41 ± 13	
Fall 74	167 ± 26 (3)	6 ± 3	3 ± 1	11 ± 5	80 ± 8
Wells Bay Low Beach					
Fall 73	148 ± 18 (2)	47 ± 3	32 ± 1	20 ± 3	
Spring 74	123 ± 3 (2)	51 ± 6	32 ± 6	16 ± 0	
Wells Bay High Beach					
Summer 73	255 ± 47 (2)	37 ± 1	26 ± 4	36 ± 3	
Spring 74	175 ± 38 (2)	48 ± 0	25 ± 1	26 ± 1	
Old Valdez					
Spring 74	91 ± 8 (2)	26 ± 4	18 ± 1	56 ± 4	
Fall 74	167 ± 8 (2)	12 ± 4	14 ± 5	74 ± 9 [b] value for combined region	
Orca Bay					
Spring 74	288 ± 65 (3)	52 ± 5	24 ± 4	23 ± 2	
Bligh Island					
Summer 73	73 (1)	25	18	57	
Fall 73	171 ± 9 (2)	31 ± 1	22 ± 4	46 ± 3	
Spring 74	249 ± 12 (5)	43 ± 3	26 ± 4	30 ± 4	
Siwash Bay					
Spring 74	105 ± 12 (3)	29 ± 9	26 ± 3	45 ± 6	
	311 ± 8 (2)	45 ± 4	36 ± 1	20 ± 6	
Fall 74	61 ± 6 (3)	53 ± 2	20 ± 5	27 ± 8 [b] value for combined region	
Cape Yakataga					
Fall 74	72 ± 16 (3)	26 ± 10	13 ± 5	12 ± 2	48 ± 17
	367 (1)	37	18	8	37
Katalla River					
Fall 74	566 ± 143 (3)	28 ± 8	31 ± 2	40 ± 14 [b] value for combined region	
MacLeod Harbor					
Fall 74	124 ± 49 (5)	22 ± 4	23 ± 3	34 ± 5	21 ± 5
Middleton Island					
Fall 74	155 ± 45 (4)	32 ± 6	36 ± 8	14 ± 1	18 ± 2
Squirrel Bay					
Fall 74	956 ± 63 (2) [c]	11 ± 4	4 ± 3	84 ± 6 [b] value for combined region	

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[a] ( ) denotes the number of samples analyzed.

[b] Phenanthrene internal standard not recovered so component amounts included in propylnaphthalene (or trimethylnaphthalene) molecular weight region.

[c] Abnormally high value for maximum hydrocarbon content not consistent with low values obtained from water analyses. This was a very adsorptive sediment requiring 5x the amount of internal standard to be seen in the gas chromatogram. This site visually appears to be quite pristine. It is under continuing investigation.

Table 46.1. Hydrocarbon Content of Sediment Samples as Expressed in Percentages by Molecular Weight Region.

Table 46.2. Water Analyses-Fall 1974 Sampling

		Percent of Total Hydrocarbons by Molecular Weight Region			
Site	Total Maximum Hydrocarbon Content (µg/kg) Obtained by Headspace Sampling	Mesitylene	Naphthalene	Propyl-Naphthalene	Phenanthrene
Dayville Mud Flats					
Surface	2.7 ± 1.0 (3) [a]	36 ± 20	21 ± 3	44 ± 19	b
10 meter	1.6 ± 0.2 (2)	38 ± 1	42 ± 2	20 ± 1	b
Old Valdez					
Surface	14.9 (1)	27	29	44	b
10 meter	0.95 ± 0.38 (3)	20 ± 6	37 ± 8	44 ± 9	b
Cape Yakataga					
Surface	11.3 ± 0.9 (3)	21 ± 10	32 ± 1	47 ± 10	b
Katalla River					
Surface	3.4 ± 1.3 (3)	21 ± 8	23 ± 3	54 ± 11	b
Anchor Cove					
Surface	8.0 ±0.1 (2)	21 ± 1	8 ± 3	8 ± 1	63 ± 4
10 meter	3.6 ± 0.4 (2)	55 ± 16	10 ± 1	14 ± 4	20 ± 11
Hinchinbrook Is.					
Surface	5.3 ± 1.8	46 ± 33	19 ± 19	27 ± 32	11 ± 2
MacLeod Harbor					
Surface	7.3 ± 0.1 (2)	53 ± 4	8 ± 2	7 ±2	31 ± 1
10 meter	30.5 (1)	57	23	6	14
	3.9 ± 1.2 (3)	76 ± 6	10 ± 3	12 ± 5	b
Middleton Island					
Surface	5.4 (1)	26	16	22	36
Siwash Bay					
Surface	3.0 (1)	41	45	13	b
10 meter	1.9 ± 0.1 (3)	40 ± 10	7 ± 2	30 ± 9	22 ± 8
Squirrel Bay					
Surface	4.5 ± 1.1 (3)	26 ± 10	8 ± 4	42 ± 18	23 ± 5
10 meter	5.1 (1)	44	4	9	44

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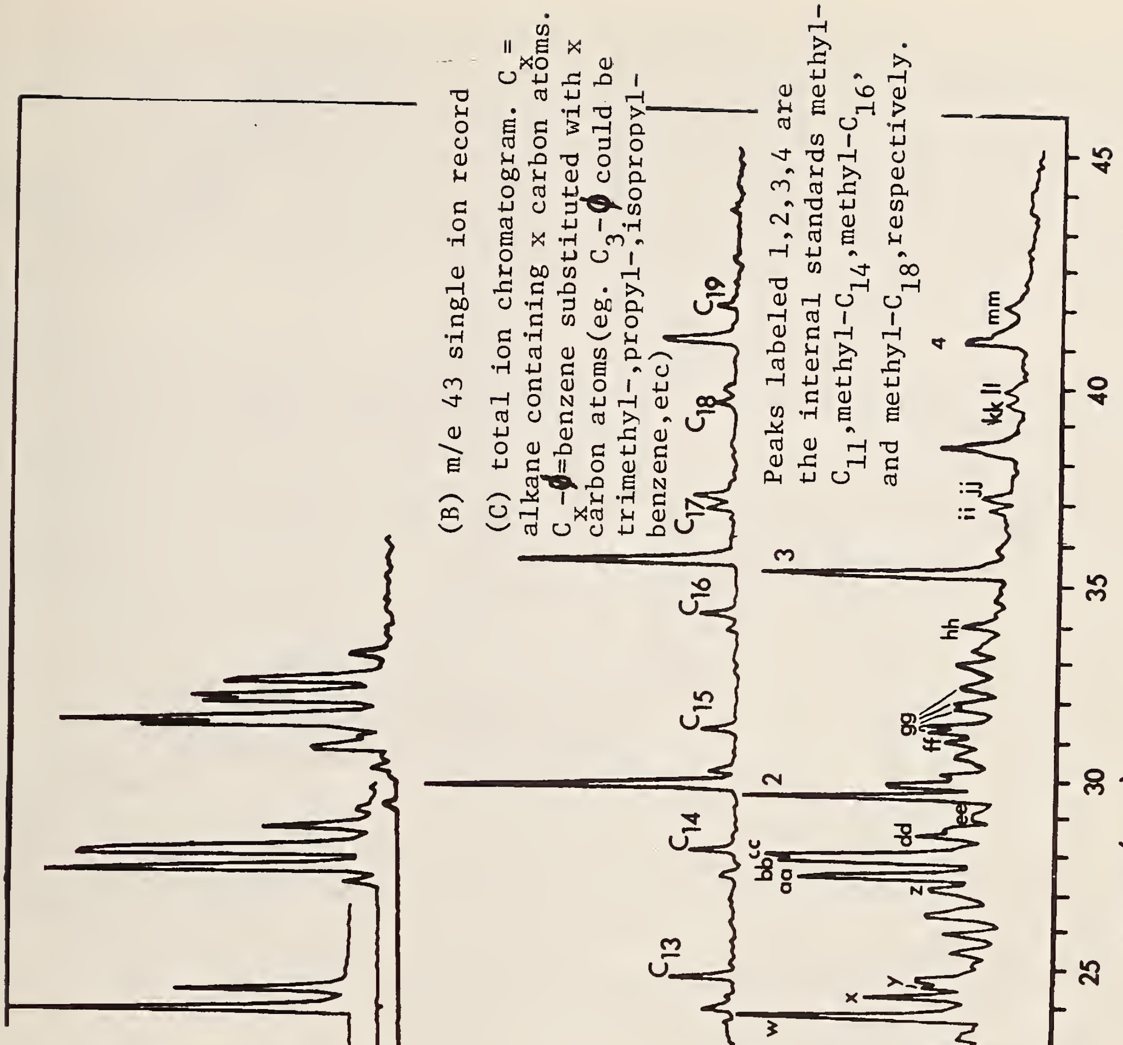
[a] ( ) denotes number of samples analyzed.
[b] Phenanthrene not included in internal standard.



(A) composite m/e 142,156 and 170 single ion records indicating presence of C_1, C_2, and C_3-naphthalenes, respectively.

(B) m/e 43 single ion record

(C) total ion chromatogram. C_x = alkane containing x carbon atoms. C_x-φ=benzene substituted with x carbon atoms(eg. C_3-φ could be trimethyl-,propyl-,isopropyl-benzene,etc)

Peaks labeled 1,2,3,4 are the internal standards methyl-C_{11},methyl-C_{14},methyl-C_{16}, and methyl-C_{18},respectively.

Figure 46.1 GC-MS analysis of Katalla River sediment

Due to the presence of petroleum hydrocarbons in the Katalla River sediment, studies are underway using this sediment as a petroleum-in-sediment interlaboratory calibration material. Large quantities of the Katalla River sediment have been collected and are being distributed to various laboratories for hydrocarbon analysis using their particular methodologies. Comparison of the interlaboratory data should provide a measure of the analytical variability among the participating laboratories.

An analytical method for the determination of petroleum hydrocarbons in various marine tissue samples has been developed in our laboratory. The method involves dynamic headspace sampling of the tissue homogenate followed by liquid chromatographic removal of the biogenic polar components prior to quantitation of the petroleum hydrocarbons using high resolution gas chromatography. Since most of the organic compounds being removed from the tissue homogenate are of biological origin, a liquid chromatographic cleanup is necessary to remove these biogenic components. Figure 46.2A is a gas chromatogram obtained from headspace sampled *Mytilus* tissue homogenate without removal of the polar biogenic components. An effective LC cleanup is achieved using a μBondapak NH_2 column (Figure 46.2B), thereby reducing the biogenic background in the gas chromatogram and allowing greater sensitivity for the individual petroleum hydrocarbon components. When using a nonpolar mobile phase such as pentane, the μBondapak NH_2 column provides a class separation similar to that obtained using a silica column, i.e., saturated hydrocarbons elute before unsaturated hydrocarbons and aromatics, and the elution volume for the aromatics increases with the number of condensed rings.

Using a nonpolar mobile phase, the biogenic compounds, which are thought to be long-chain aliphatic alcohols, are retained on the polar LC column. These compounds are removed from the column by increasing the polarity of the mobile phase. The polar biogenic components which were retained on the column during the LC cleanup are shown in Figure 46.2C after removal from the column using methanol.

Analyses using this method are presently being performed to determine the baseline hydrocarbon levels in *Mytilus* tissue collected at sites in Prince William Sound and Northeastern Gulf of Alaska.

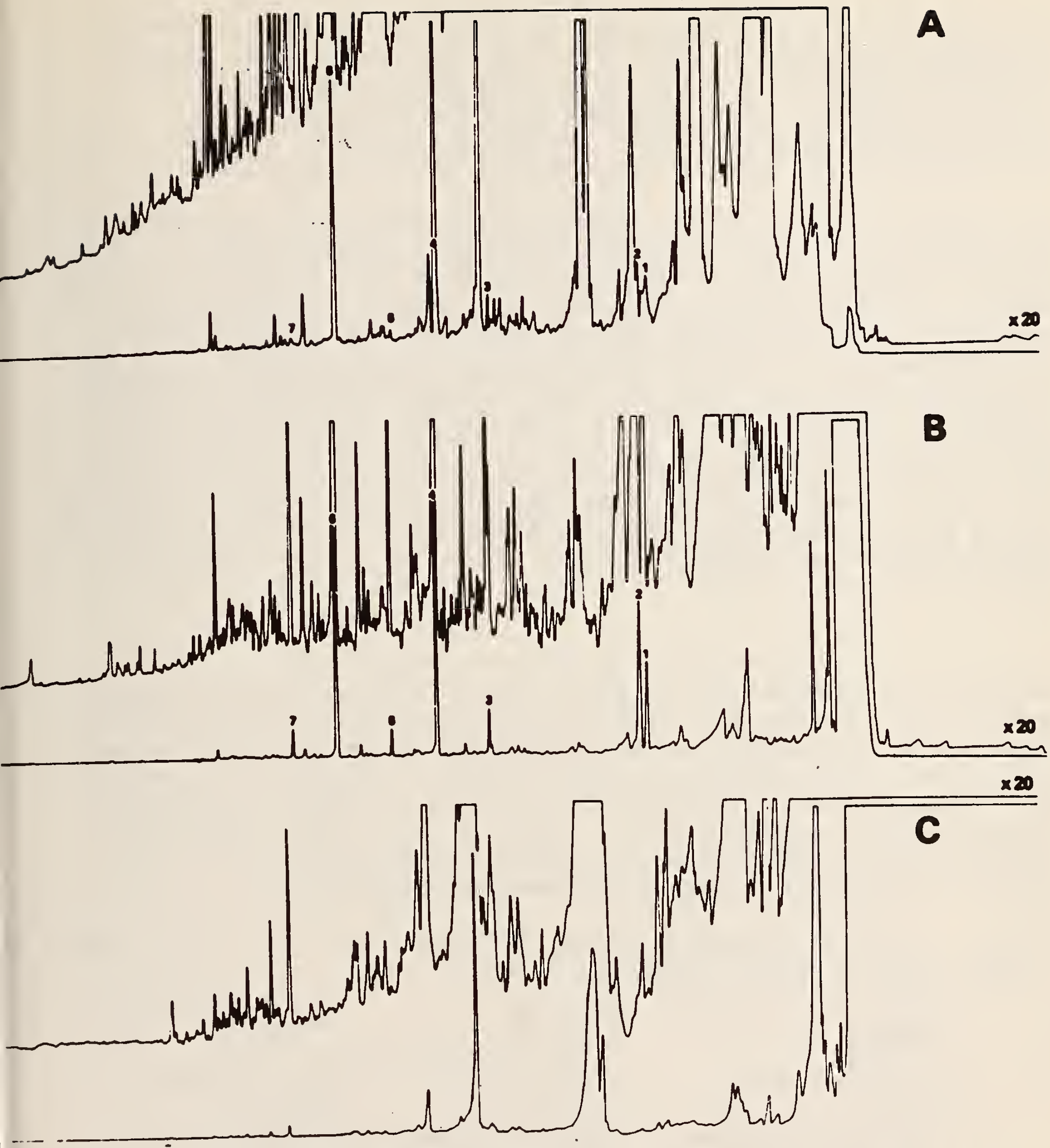


Figure 46.2 Gas chromatographs of headspaced sampled Mytilus tissue with 50μg crude oil added without any LC cleanup of the TENAX-GC pre-column(A) and with LC cleanup using a μBondapak NH$_2$ column (B). Numbered peaks correspond to the internal standard compounds each added at the ∿50μg/kg level(1=2-methylundecane, 2=naphthalene, 3=5-methyltetradecane, 4=trimethylnaphthalene, 5=7-methylhexadecane, 6=phenanthrene, and 7=2-methyloctadecane. Gas chromatogram of biogenic compounds removed from LC column with methanol (C).

Fluorescence spectroscopy has been investigated as a means of achieving added sensitivity and selectivity for liquid chromatographic detection of polynuclear aromatic hydrocarbons (PAH's). Fluorescence LC detection has been particularly useful for the identification of PAH's of suspected petroleum origin in sediment and marine tissue.

Extracts of two sediment samples with known petroleum exposure were found to contain relatively high concentrations of a single PAH that may be useful as a petroleum marker compound. These sediments were collected at a tanker facility in Freeport, Grand Bahamas and on the beach in Santa Barbara, California (see Figures 46.3 and 46.4, respectively). Liquid chromatographic analysis of the sediment extracts indicated a marker compound content of ~150 ppb at the Bahamas tanker facility and ~13 ppb at the Santa Barbara beach. Extracts of sediment from a control site in the Prince William Sound in Alaska showed very little evidence of the marker compound ($<$ 1.3 ppb), which has been tentatively identified as benzo(a)-pyrene based on chromatographic retention, mass spectrometric, and fluorescence data.

Measureable quantities of PAH's have also been identified in marine tissue samples using fluorescence detection. Samples of oysters collected in the Elizabeth River in Virginia were extracted and analyzed for PAH's by LC. Figure 46.5 compares the chromatograms obtained for UV 254 nm detection (A) and fluorescence detection (B). Peaks 1 and 2 were identified on the basis of retention time and fluorescence spectra as chrysene and benzo(a)pyrene, respectively.

Figure 46.1 C. Identifications followed by "?" are not definite due to incompletely resolved spectra.

a-C_2- cyclohexane
b-C_2-ϕ
c-C_2-ϕ
d-C_3-thiophene
e-$\underline{n}$-C_9
f-C_3-cyclohexane
g-propyl-ϕ
h-C_3-ϕ
i-C_3-ϕ
j-C_3-ϕ & C_4-thiophene
k-C_4-thiophene
l-$\underline{n}$-C_{10}
m-C_3-ϕ
n-C_4-cyclohexane
o-C_4-ϕ
p-C_5-thiophene ?
q-$\underline{n}$-C_{11}
r-C_4-ϕ
s-C_5-cyclohexane
t-C_2-decalin
u-$\underline{n}$-C_{12}
v-C_6-cyclohexane
w-C_1-naphthalene
x-C_1-naphthalene
y-$\underline{n}$-C_{13}
z-ethyl-naphthalene
aa-C_2-naphthalene
bb-$\underline{n}$-C_{14} & C_2-naphthalene
cc-C_2-naphthalene
dd-C_2-naphthalene
ee-ethyl-naphthalene ?
ff-$\underline{n}$-C_{15}
gg-C_3-naphthalene
hh-$\underline{n}$-C_{16}
ii-$\underline{n}$-C_{17}
jj-pristane
kk-$\underline{n}$-C_{18}
ll-phytane
mm-$\underline{n}$-C_{19}

Figure 46.3 A. Liquid chromatograms of bottom sediment extract (solid line) and beach sediment extract(dotted line) using ultraviolet detection at 254 nm; B. Fluorescence emission spectra of largest peak in bottom sediment chromatogram (dashed line) and reference sample of benzo(a) pyrene (solid line); excitation-290nm.

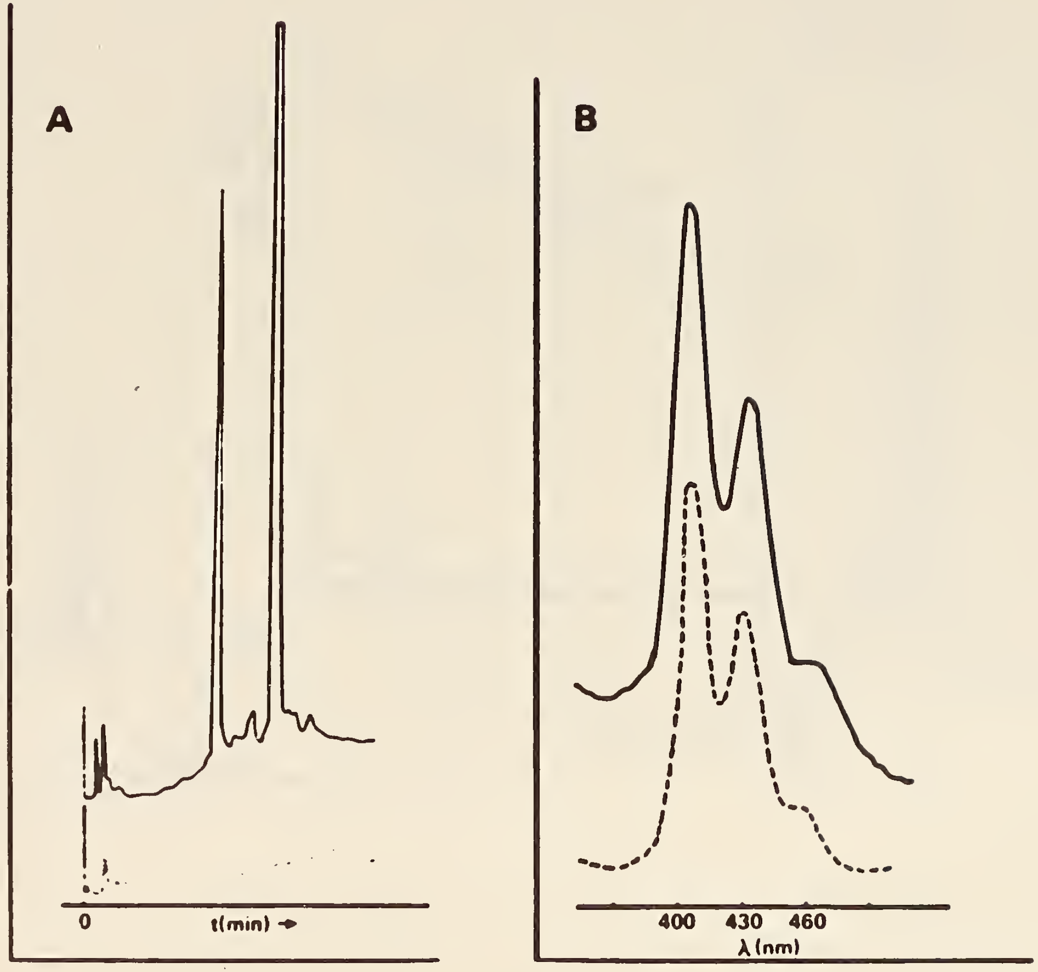


Figure 46.4 Santa Barbara sediment. A. Liquid chromatogram of extract of sediment; B. Fluorescence emission spectra of peak 1, excitation -300 nm.

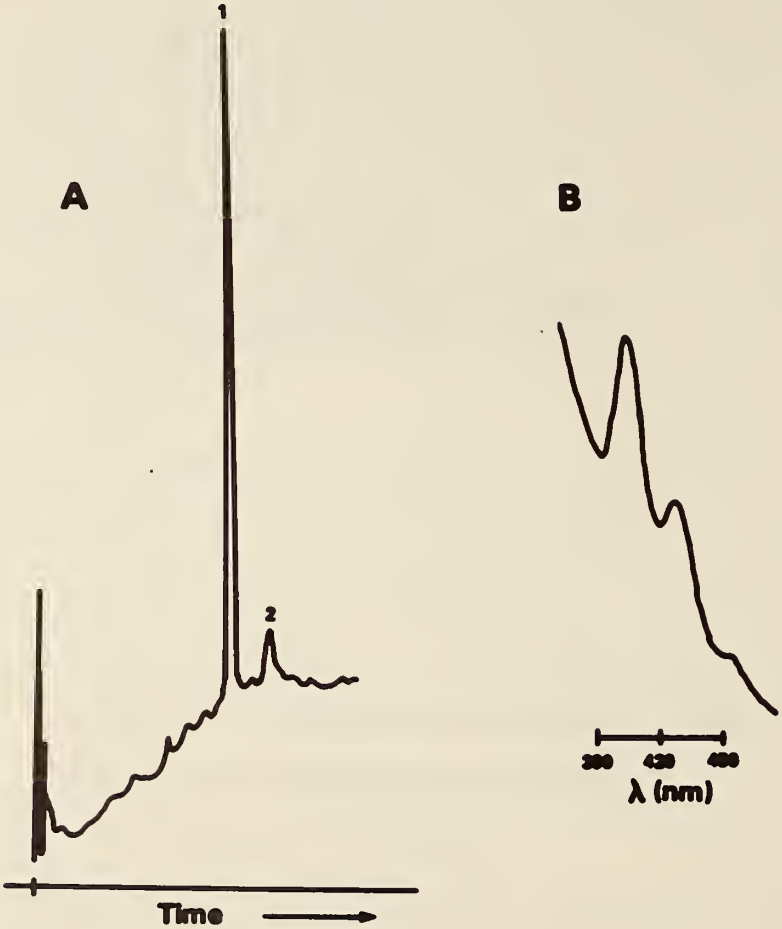
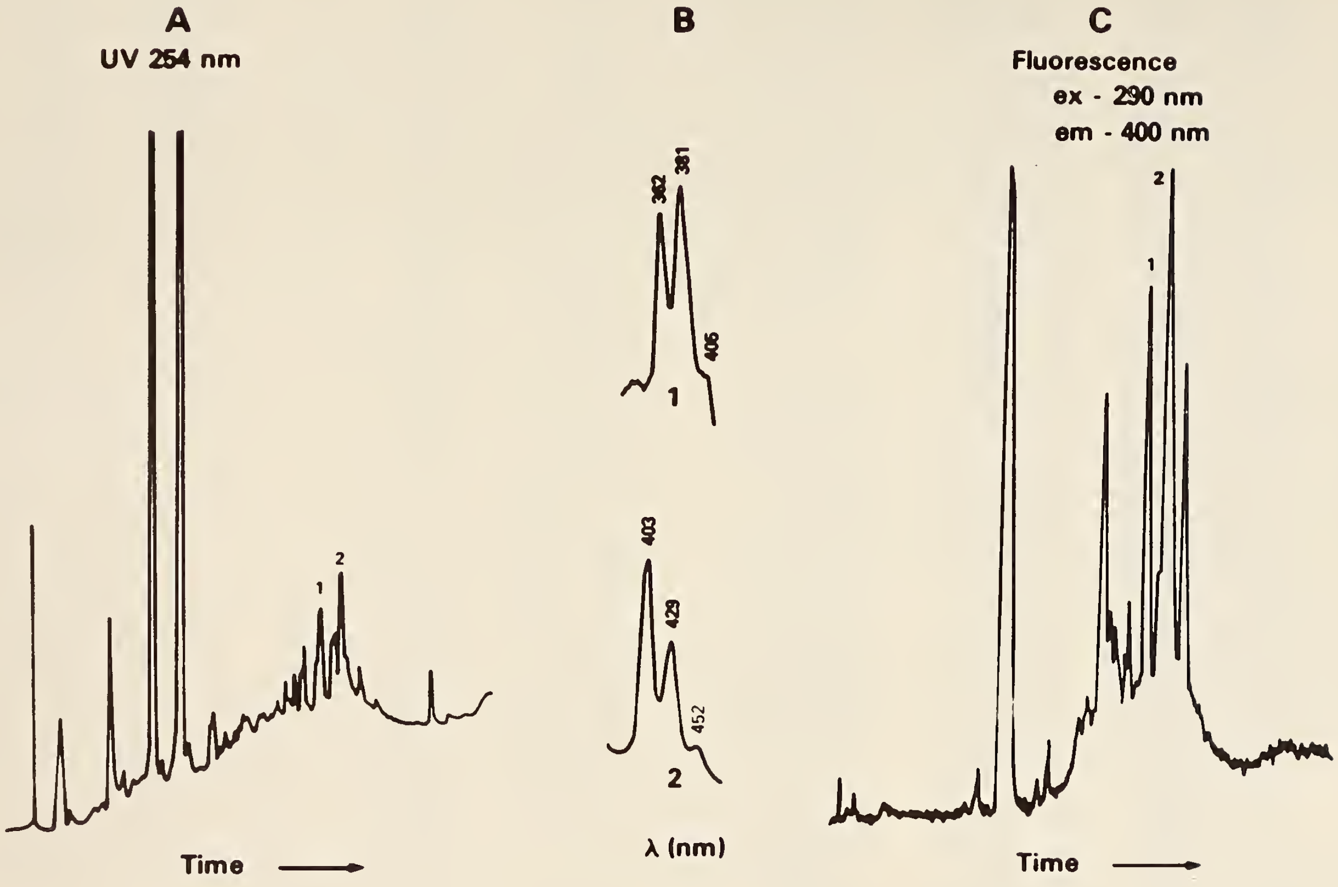


Figure 46.5 Liquid chromatograms of an extract of Elizabeth River oysters using UV detection at 254 nm (A). and Fluorescence emission at 400 nm with 290 nm excitation (B). Fluorescence spectra for peaks 1 and 2 are shown with wavelengths of major peaks given in nm.



47. Organochlorine Analyses

Project Leaders: S. N. Chesler and H. S. Hertz, Analytical Chemistry Division

Objectives

1. Set up a laboratory for organochlorine (RCl) analysis.
2. Procure equipment and other objects necessary to implement ASTM procedure for the analysis of polychlorinated biphenyls (PCB's), ASTM designation D3304-74.
3. Using D3304-74 obtain acceptable blanks $(< .1\%)$.
4. Analyze samples supplied by Monsanto (consisting of distilled and river waters spiked with Aroclor 1254 or 1016).
5. Note shortcomings in ASTM D3304-74 procedure.
6. Familiarize ourselves with proper laboratory procedures for RCl analyses.

Accomplishments

1. Single laboratory module (B-105/222) was cleaned and Teflon coated bench coverings applied to all work surfaces. The existing exhaust hood was modified to accept the evaporation apparatus required by D3304-7.
2. Approximately $3K spent in obtaining extraction and evaporation glassware. A linearized electron capture (EC) gas chromatographic instrument was set up and checked out.
3. To obtain 0.1% blanks, it was necessary to follow the criteria below:
    a) Prior to use, all glassware must be soap and water washed, then be immersed in a hot acid bath (H_2SO_4 at 105°C) for at least one hour, and finally rinsed with hydrocarbon-free water.
    b) Glass wool and Na_2SO_4 used in D3304-74 must be cleaned by exhaustive soxhlet extraction (minimum of 18 h) with pesticide grade hexane.

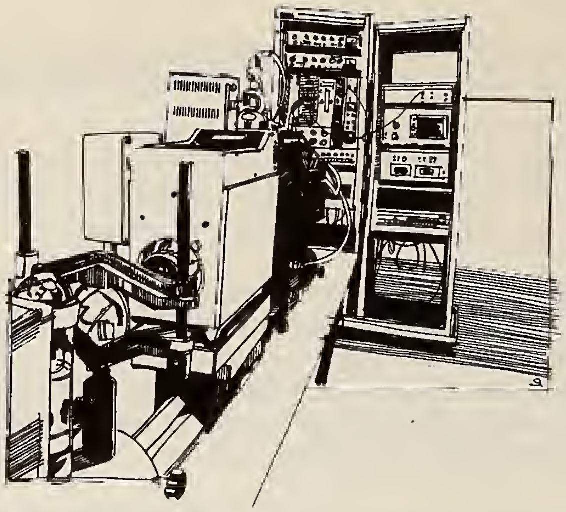
  c) The clean Na_2SO_4 must be used quickly (1 week) otherwise it will pick up contaminants and cause high blanks.

  d) Hexane extracts containing PCB's at mg levels are not stable for long periods of time. Thus new standards must be prepared at least weekly.

4. Results of Analyses were not obtained due to the deterioration of the water samples provided by Monsanto. The samples were exposed to moderately high (~50°C) temperatures when refrigeration equipment in which they were stored failed. We postulate that this caused deterioration of PCB containing samples.

5. The major shortcoming of D-3304-74 is the lack of detailed protocol for clean-up of glassware, chemicals, and apparatus necessary to achieve consistently low blanks. The data reduction section of D-3304-74 is confusing.

6. We find that it is not a trivial undertaking to set up and run RCl samples. Great care is needed to maintain the integrity of the analyses undertaken. We feel that NBS cannot undertake to realistically perform state-of-the-art RCl analyses without a concentrated and well run experimental program.



48. Fate and Effects of Oil Discharged on the Marine Environment

Project Leader: S. Wasik, Physical Chemistry Division

Other Personnel: F. P. Schwarz, R. N. Boyd, R. L. Brown, J. I. Minor, T. Krishnamurthy

Objective

To provide a technical basis to formulate, promulgate, and defend international regulations concerning permissible discharges of oil from ships. More specifically, these objectives are: (1) to measure the partitioning of petroleum products in the environment, (2) to develop methods, based on physical and chemical concepts, for sampling, handling, and analyzing hydrocarbons in an aquatic environment, and (3) to evaluate the sensitivity and selectivity of spectrofluorimetry for measuring aromatic hydrocarbons in water and to apply this technique to elucidate the physical and chemical properties of aromatic hydrocarbons in aqueous systems.

Progress

The Partitioning of Petroleum and Petroleum Products in the Environment: Three methods have been developed for determining the partition coefficients and solubilities of hydrocarbons in fresh and sea water. These methods can be used to measure partition coefficients in the range of 0.01 to 100 over a temperature range 0-25°C. The first method [1,2,3] determines by gas chromatography, the relative hydrocarbon concentration of the gas phase in equilibrium with a liquid or solid. A known volume of the gas phase is then purged out of the apparatus and replaced with clean air. The relative hydrocarbon concentration in the gas phase is measured after the second equilibrium. The partition coefficient is calculated from the area ratios of the solute peaks and the volume of the gas and liquid phases.

The second method consists of extracting dissolved hydrocarbons from a sea-water extract with small hydrogen bubbles generated electrolytically from a gold electrode located in the bottom of a cylindrically shaped cell [3,11]. The partition coefficient is determined by measuring the decrease in hydrocarbon concentration as a function of the volume of hydrogen bubbled through the cell.

A third method for determining the partitioning of hydrocarbons between water and air was developed for the high molecular weight polycyclic aromatics [13]. This method is similar to the first method except fluorimetry is used to determine the hydrocarbon concentrations in the water phase.

Using these methods, the partition coefficients and solubilities of most of the aromatic hydrocarbons of interest in oil spill studies have been determined as a function of temperature and salinity.

A method [12] has been developed for determining the partition coefficient of aromatic solutes between water and a lipid phase (1-octanol). This method also uses fluorimetry to determine the hydrocarbon concentration in the water phase.

Development of Methods for the Analysis of Trace Amounts of Hydrocarbons in the Aquatic Environment: A method was developed for the analysis of trace amounts of hydrocarbons in sea water using the concept of extracting the organic material by electrolytically generated hydrogen [4,8]. The advantages of this method are: (1) the hydrocarbons are extracted from the analytical cell as hydrocarbon groups, (2) no impurities are added to the sea water by the extracting solvent, and (3) a minimum of sample handling is required for analysis.

In conjunction with this work, new types of chromatography columns were developed in order to separate the aromatic hydrocarbons. A liquid crystal column [10] was used to separate the naphthalene homologues and a solid silver nitrate column [9] was used to separate the alkyl-substituted benzenes.

A gas-chromatography plasma detector was built for elementary and deuterium analyses. This detector will be used in stable isotope analysis to determine bio-concentrations and hydrocarbon breakdown in live fish. This detector will also be used to determine vapor pressures of polycyclic aromatics.

Sensitivity and Selectivity of Spectrofluorimetry: A spectrofluorimeter was assembled using photon counting techniques. Fluorescence spectra, quantum yields, and sensitivities were determined for fine representative polycyclic aromatic hydrocarbons in aqueous solutions to ascertain the applicability of using this technique for pollution studies [5,6] .

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49. DDT Propagation Models

Project Leaders: A. J. Goldman and L. S. Joel, Applied Mathematics Division

Objective

The interagency Federal Working Group on Pest Management, in connection with its efforts to test existing mathematical models of DDT and develop superior models as needed, requested support to the Ad Hoc Committee on Mathematical Models of its Research Panel. The present project provides the support component of mathematical modeling and analysis pledged by the Director of NBS through DoC's Deputy Assistant Secretary for Environmental Affairs. Its objective is to assist a significant interagency effort to determine the suitability of current mathematical models and data for predicting and evaluating residues in soil, water, and air of pesticides (specifically DDT), to create improved models and secure additional data as required, and to identify critical research needs in this field.

Approach

Mathematical analyses are performed of the logical consistency, algorithmic quality and data-fitting capability of proposed or newly synthesized models, with special attention to the sensitivity of outputs to uncertainties in data or model structure. Related numerical computations are funded by EPA (Project 2050407).

Progress

At the Working Group's request we have focused on a particular model which applies J. W. Forrester's "Systems Dynamics" approach and the associated "DYNAMO" simulation language to the construction of computerized ecosystem models. The model is documented in [1].

The model uses a set of difference equations to trace over time the flow and accumulation of DDT among/in 5 major ecological "compartments" (soil, air, rivers, oceans and fish), each considered as a single homogeneous worldwide aggregate. The flow is triggered by application of DDT, and its analysis stops short of considering the takeup of DDT by life forms higher than fish.

We recognized 5 goals: (a) to obtain and check-out a DYNAMO compiler compatible with the NBS computer and its operating system, (b) to check that the Systems Dynamics model accurately represented the differential-equations system which follows directly from the defining transfer relationships, (c) to identify the most critical model assumptions and parameters in terms of sensitivity of outputs, (d) to identify the model assumptions most questionable because of absence of corroborating data (or presence of alternative plausible hypotheses also compatible with data), and (e) to identify critical directions and data requirements for refining this very crude model.

Goals

(a) An updated compiler, DYNAMO II_F has been acquired and is at present undergoing acceptance test and integration into the executive system of NBS' Univac 1108 computer.

(b) Two rudimentary extensions of the DYNAMO model have been initiated: A partition of "soil" into two compartments to study the effects of the application of DDT in one part of the world's land mass on accumulation elsewhere and the addition of an aggregated compartment, representing food chains above the level of fish, to furnish a source of feedback (through mortality and excretion) from what was previously treated as a sink.

Further disaggregation to isolate regions with apparently high relative concentrations of DDT such as estuarine waters and lakes will be attempted.

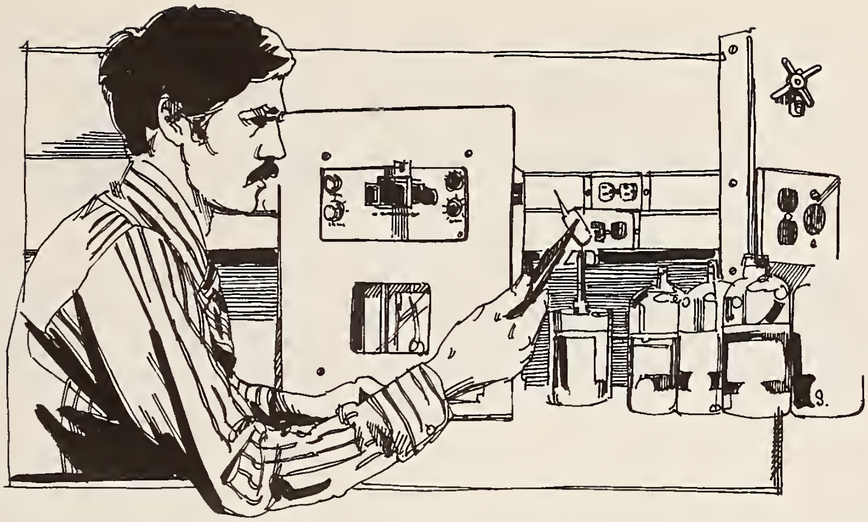
(c) Sensitivity analysis of the system through parameter variation in model runs (in progress) will be supplemented by further mathematical treatment of the differential equations.

Additional modeling systems, e.g., CSMP will be examined and compared with DYNAMO.

(d) Redefinition of some model components and reorganization of outputs, e.g., calculation of concentrations in place of mass levels, will be made to facilitate comparison of modeling results to those from other models.

Future Plans

We are intensifying our efforts to develop guidelines for: The selection and testing of mathematical procedures and computer software for modeling and the determination of levels of model aggregation and data precision consistent with given modeling objectives.



50. Reactor Effluent and Environmental Radioactivity Standards

Project Leader: J. M. R. Hutchinson, Center for Radiation Research

B. M. Coursey, L. L. Lucas, P. A. Mullen, J. R. Noyce, F. J. Schima, M. P. Unterweger

Objective

The objective is to improve the accuracy of measurements of radioactivity in the environment and in the effluents from nuclear facilities. In order to accomplish this, an immediate goal is to make all such measurements in the United States either directly or indirectly traceable to the National Bureau of Standards.

Approach

Current activities on this project can be grouped into the following three categories: (1) Establishing traceability of radioactivity measurements performed by the Nuclear Regulatory Commission (NRC) and Environmental Protection Agency (EPA); (2) Development and Production of radioactivity sources calibrated for activity or emission rate and issued as standard reference materials (SRMs) to be used as either test sources or for the calibration of detectors by environmental monitoring laboratories. Much of the work in developing radioactivity standards of "heavy element" radionuclides, including those in the natural decay chains has been supported under an EPA sponsored "energy program". Milestones are shown in Table 50.1; (3) Performance of developmental work aimed at maintaining a "state-of-the-art" measurement capability and dissemination of information through committees, publications and talks.

TABLE 50.1

RADIOLOGICAL POLLUTANT ASSURANCE[a]

Performing Agency: National Bureau of Standards
(EAP I.D. No.: 77 BCN)

	(Funding $K)									
Task 1. Radiological Standard Reference Materials	FY[b] 76	FY 77	FY 78	FY 79	FY 80	FY 1976	FY 1977	FY 1978	FY 1979	FY 1980
1.1 Establish Lab Facility	40[c]	--	--	--	--	—Δ				
1.2 ^{210}Po Standard	10[d]	--	--	--	--	—Δ				
1.3 ^{226}Ra Soil, Mixed Gamma Solution, ^{239}Pu	41[d]	15	--	--	--	—	—Δ			
1.4 Mixed Gamma Soil	--	20	5	--	--		—	—Δ		
1.5 ^{230}Th, ^{238}Pu, ^{241}Pu	--	15	10	--	--		—	—Δ		
1.6 ^{241}Am, ^{242}Am, ^{235}U, ^{238}U	--	--	35	15	--			—	—Δ	
1.7 ^{210}Pb, ^{232}Th, ^{243}Cm, ^{244}Cm	--	--	--	35	30				—	—Δ
Totals	91	50	50	50	30					

[a] Issuance of all SRM's are subject to satisfactory performance as defined by NBS SRM criteria.

[b] This is the only one of the three subagreements in which funds from EPA FY's 75 and 76 will be expended entirely in the NBS FY 76.

[c] Funding from EPA FY 75 Allocation.

[d] Funding from EPA FY 76 Allocation.

Traceability. Since 1971 we have engaged in a traceability study with the Health Services Laboratory (HSL) of the U. S. Atomic Energy Commission (AEC) in Idaho Falls. We have also, recently initiated a traceability program with the Quality Assurance Branch of the U. S. Environmental Protection Agency (EPA). Agreements have been reached specifying how traceability to NRC and EPA is to be established and maintained.

These agreements require that NBS provide approximately 15 test samples to each of the two laboratories and also to perform some testing of NRC and EPA sources. The status of the projects for the 1974-1976 period are summarized in Table 50.2 for NRC and Table 50.3 for EPA.

Standard Reference Materials. The following SRM's have been developed over the three year period.

- Low-Energy-Photon-Emission Rate Standards ("Point Source")
    - Iron-55
    - Strontium-85
    - Cadmium-109
    - Iodine-125
- Natural Matrix Standards
    - River sediment
    - Homogeneous river sediment
    - Mancos shale (in preparation)
    - Dead water (in preparation)
    - Radon Blanks (in preparation)
- Gaseous Standards
    - Argon-37
    - Argon-39
    - Krypton-85
    - Xenon-127 (in preparation)
    - Xenon-133
- Alpha-Particle-Emitting Solution Standards
    - Americium-241
    - Americium-243
    - Plutonium-239
    - Plutonium-242

TABLE 50.2

TRACEABILITY TESTS WITH HEALTH SERVICES LABORATORY, USNRC

Category	FY 1974		FY 1975		FY 1976	
	Parent Radionuclide	Cert. Date	Parent Radionuclide	Cert. Date	Parent Radionuclide	Cert. Date
Ia Mixed Solution Sources Containing γ-Ray Emitting Radionuclides			^{51}Cr	Aug 75	^{51}Cr	Aug 75
			^{54}Mn	Aug 75	^{65}Zn	Aug 75
			^{88}Y	Aug 75	^{88}Y	Aug 75
			^{137}Cs	Aug 75	^{137}Cs	Aug 75
			^{139}Ce	Aug 75	^{139}Ce	Aug 75
Ib Individual Test Solutions Containing γ-Ray Emitting Radionuclides	^{51}Cr	Apr 74	^{54}Mn	Mar 75	^{22}Na	
	^{75}Se	Apr 74	^{65}Zn	Oct 74	^{57}Co	Dec 75
	^{203}Hg	Oct 73	^{109}Cd	Jul 74	^{60}Co	Jul 75
			^{110m}Ag	Jun 74	^{85}Sr	Sep 75
			^{134}Cs	May 75	^{198}Au	Dec 75
II Beta-Particle-Emitting Radionuclides			^{14}C	Jan 75	^{32}P	Nov 75
			^{90}Sr	Jul 75	^{36}Cl	May 76
	^{89}Sr/ ^{90}Sr	Apr 74			^{63}Ni	May 76
III Alpha-Particle-Emitting Radionuclides			^{239}Pu	Jun 75	^{148}Gd	Mar 76
			^{242}Pu	Mar 75	^{210}Po	Feb 76
			^{243}Am	Jan 75	^{241}Am	Jun 76

Table 50.2 (cont'd)

Category	FY 1974		FY 1975		FY 1976	
	Parent Radio-nuclide	Cert. Date	Parent Radio-nuclide	Cert. Date	Parent Radio-nuclide	Cert. Date
IV Tritium			^{3}H	Apr 75	^{3}H	May 76
V NBS Tests of HSL Standards	^{54}Mn	Nov 73				
	^{60}Co	Nov 73				
	^{65}Zn	Nov 73				
	^{88}Y	Nov 73				
	^{89}Sr	Aug 73				
	^{90}Sr	Nov 73				
	^{137}Cs	Mar 74				
	^{144}Ce	Nov 73				

Table 50.3

TRACEABILITY TESTS WITH EPA REFERENCE LABORATORY QUALITY ASSURANCE BRANCH, EPA NERC-LV

		FY 74	FY 75[(a)]	FY 76
EPA Standards Measured at NBS	γ	^{54}Mn ^{60}Co ^{65}Zn	^{131}I	
	β	^{89}Sr ^{90}Sr	^{3}H	(^{89}Sr)
NBS Test Sources Measured by EPA	γ	^{51}Cr ^{75}Se ^{137}Cs ^{203}Hg	(^{59}Fe) ^{60}Co ^{109}Cd ^{110m}Ag	(^{85}Sr) ^{134}Cs
	β	^{89}Sr/^{90}Sr	(^{14}C)	(^{32}P) (^{90}Sr)

(a) Parentheses indicate that measurements are in progress.

- Beta-Particle-Emitting Solution Standards and Test Samples

    Strontium-89
    Strontium-90
    Mixed ^{89}Sr + ^{90}Sr (test sample)

- Gamma-Ray-Emitting Solution and "Point Source" Standards and Test Samples

    Mixed-gamma-ray-emitting standards
        (i) solution in 50 ml and 450 ml sizes
        (ii) Point source standards
    Europium-152
    Cesium-134

Developmental Work and Other Activities

1. An interlaboratory intercomparison by 14 laboratories was conducted by NBS using mixed-radionuclide-test samples.

2. To enable us to make measurements on such materials as fresh water sediment, we have had to develop our low level measurement capability. In this regard we have developed, tested and are presently using an anti-compton, anti-coincidence shielded Ge(Li) system, we have upgraded the Omnigard low level beta particle measurements systems, and have installed and are using a relatively low level liquid scintillation system.

3. In 1974, we surveyed European laboratories to determine whether mutually beneficial, joint programs could be developed which related to measurements of low level radioactive effluents from nuclear power reactors.

4. Standardization of solutions of the alpha particle emitting radionuclides ^{210}Po, ^{242}Pu and ^{243}Am have been accomplished using the newly developed liquid-scintillation counter.

5. New standards and method for measurement of reactor off gases by gamma ray spectrometry have been developed.

6. Committee involvement includes work on (a) the Interagency Committee on Plutonium and Other transuranium elements (b) NCRP SC18A (which is developing a revised version of NBS Handbook 80) (c) ANSI N42.2 Subcommittee on Radioactive Reference Standards, (d) International Committee for Radionuclide Metrology, Low Level Techniques Group.

A seminar will be held in Paris in October to determine what the needs are in the metrology of environmental radioactivity. It is hoped that the recommendations from the seminar will provide a basis for a coherent international effort in the development of environmental radioactivity standards.

7. A technique for the spiking of sediment, which is then homogenous in radioactive concentration, has been developed.

8. NBS has distributed many standards (Table 50.4) directly to state laboratories in line with our desire to develop an active "states program".

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Table 50.4

NBS STANDARDS DISTRIBUTED TO STATE LABORATORIES

Calendar Year	Type of Standard	No. of States	Sponsoring Agency
1973	Xenon-133 Gas	20	AEC(NRC)
1975	Krypton-85 Gas	19	NRC
	Mixed Gamma-ray Solution 1	25	EPA
	Mixed Gamma-ray Solution 2	22	EPA
	Polonium-210	39	EPA
1976	Xenon-131m	19	NRC
	[a] Mancos Shale		EPA
	[a] Plutonium-239		EPA
	[a] Xenon-133 Gas		NRC
	[a] Xenon-127 Gas		NRC

[a] In preparation.

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J. M. R. Hutchinson, Radioactivity Standards and Traceability Programs at NBS, Health Physics Instrumentation and Monitoring, A Symposium Sponsored by the New Jersey Chapter, Health Physics Society, South Plainfield, New Jersey, March 24, 1976.

51. Radioactivity Decay Schemes

Project Leader: D. Hoppes, Applied Radiation Division

Objective

This project aids the determination of radioactive pollutants by supplying decay scheme information and techniques necessary for the preparation and use of radioactivity standards.

Approach

The efficiency versus energy of several radiation detector systems appropriate to different radiations and energy ranges are calibrated with present supposedly well-known standards, furnishing a check of the consistency of existing decay schemes, calibrations, and techniques. These detectors are then used to check discrepant values and determine the intensity of radiations in other nuclides. For a given nuclide, these data, together with direct coincidence measurements, determine the fraction of the total nuclear decays represented by any one radiation.

Progress

The application of NRC guidelines requiring the quantitative identification of detectable gamma-ray-emitting nuclides in nuclear power plant effluents is leading to extensive use of spectroscopy-grade equipment in the field. During the past year our development of calibrated gamma-ray detectors has meshed with a program in the Radioactivity Section to supply standards for calibrating and testing such effluent-checking detectors. We developed accurate gamma-ray intensity analysis methods; searched all source materials for impurities; compared (with about 1% accuracy) various dilutions and nuclides of similar energy; and checked multi-component standards for possible difficulties in analysis. In turn, the constancy of our detectors and the applicability limits of our analysis schemes were under continual scrutiny.

The calibration of a stable Ge(Li) gamma-ray spectrometry system was continued with the addition of efficiency points for ^{51}Cr, ^{54}Mn, and ^{65}Zn. A simple computer-generated curve now relates the counting efficiency at 19 different measured energies from 279 to 1836 KeV, with a mean deviation of 1%. Discrepant points are being investigated before application of this efficiency curve to the analysis of data in hand for

^{110m}Ag, ^{75}Se, ^{125}Sb, and ^{133}Ba. Measurement of a ^{89}Sr source calibrated as to total decay rate led to the determination of a gamma fraction of (.0102 ± .0010)%.

A pure germanium x- and gamma-ray system for the energy region 20 to 400 KeV was secured and used to compare the emission rates from standards of ^{241}Am, ^{125}I, ^{109}Cd, ^{57}Co, ^{203}Hg, and ^{113}Sn- ^{113m}In. This calibration was used to check the relative intensity of several gamma rays from multiple-gamma-ray-emitting nuclides (^{75}Se, ^{169}Yb, ^{133}Ba). A calibration of the total disintegration rate of an ^{169}Yb source was made by summing the contributions of all major gamma rays.

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The projects covered in this report deal specifically with:

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Research leading to development of SRM's (Standard Reference Materials) or other means for ensuring the accuracy of air measurement methods.

Development of laboratory methods with improved accuracy, sensitivity and specificity for air pollution measurements.

Generation, evaluation, compilation and dissemination of data and technical information needed to relate the substances emitted from sources of pollution to those found in the atmosphere after chemical reactions have occurred.

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Water--

Evaluation of the accuracy of methods for measuring water velocity and flow in open and closed channels.

Development of radioactivity standards.

Development of Standard Reference Materials for evaluating the accuracy of instruments and methods for measuring the concentration of pollutants in water and sediments.

Measurement evaluation and compliation of physical and chemical properties of of known pollutants.

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