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Science & Technology

✓ JUNE 1977



Air monitoring
544-551

Designed for indoor or outdoor use, these precision instruments sample gases in ambient air . . . accurately

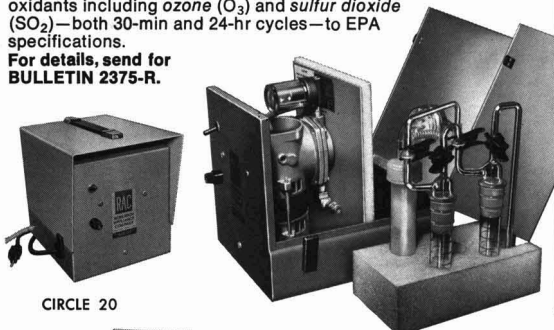
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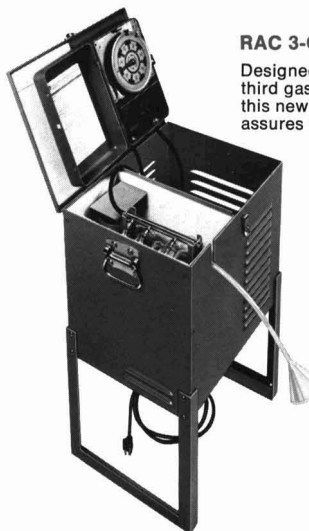
CIRCLE 20

RAC 3-GAS SAMPLER

Designed to sample SO_2 , NO_2 and a third gas (optional) simultaneously, this newly-developed instrument assures maximum accuracy for SO_2 sampling at ambient temperatures ranging from -25 to $50^\circ C$. It features a unique solid-state thermoelectric cooling-heating system (patent pending) that maintains the SO_2 reagent between 7 and $17^\circ C$, thereby preventing the loss of sample that occurs when the ambient temperature reaches/exceeds $20^\circ C$.

For details, send for BULLETIN 2441.

CIRCLE 21



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CIRCLE 22



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CIRCLE 23



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CIRCLE 24



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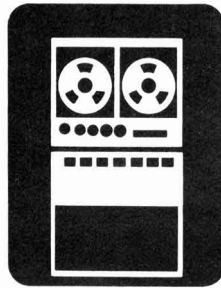
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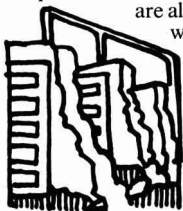
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26. JUN. 2520

Coke ovens, blast furnaces are monitored for personnel safety.

Steel mills often buy hundreds of the MSA CO alarms on a "standing order" basis to provide dependable 24-hour protection for their workers.

Just as important to the mill operator is the ease of maintenance of the 704 CO Alarm. It operates reliably under conditions which are often corrosive, dusty, hot and humid. A protective system which filters out contaminants can be replaced in 15 minutes when needed.

In many steel mills, the sensor units of the CO alarms are placed at potential points of concentration. Alarm units



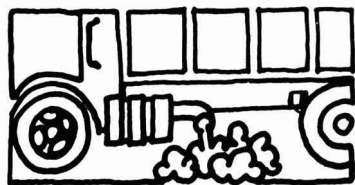
are also located there to warn workers of dangerous conditions.

Then the indicator and control circuitry for a number of CO alarms are gathered into one central control panel for easier

and more efficient monitoring. Backup audible and visual alarms, along with automatic output functions (such as startup of fans or machinery shutoff), are located at the control panel. This provides the operator with greater flexibility and control and reduces manhours required to monitor instruments.

MSA also supplies a wide variety of other protective equipment to coke oven and blast furnace workers, such as Series 510 Combustible Gas Analyzers, LIRA infrared analyzers, respirators and personal samplers for desirable air quality. Ask your MSA representative for details.

Garages, loading docks and tunnels are major CO sources.

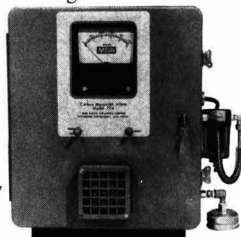


Wherever carbon monoxide can build up to peak levels, either continuously or occasionally, you will find MSA CO alarms on duty. A typical installation is

New Model 704 Carbon Monoxide Alarm. The monitor whose time has come.

NIOSH has reported that the potential for exposure to CO in the workplace is greater than for any other single physical or chemical agent. New requirements make it essential that both spot and continuous monitoring and warning of hazardous CO concentrations be installed to guard workers.

The new Model 704 CO Alarm from MSA will monitor carbon monoxide in the atmosphere continuously and automatically, with minimum attention or maintenance. And the 704 will measure two different ranges of CO: 0 to 100 parts per million (ppm), and 0 to 500 ppm. Its accuracy and alarm system allow you to meet re-



quirements for CO monitoring in ambient air. An Air-Line Adapter Kit permits monitoring for CO in compressed-air lines supplying respiratory devices.

The 704 CO Alarm is an improved version of MSA's 701 detector that has served for years in thousands of installations such as coke ovens, blast furnaces, automotive test facilities, garages, tunnels, chemical plants, petroleum refineries and industrial boiler operations.

The 704 CO Alarm switches automatically from the low to high range. Alarm contacts can be set on either range for a complete system of warning and ventilation controls, as well as process shutdown where desired. The system can be customized for various output functions with a simple digital-output function selector board. Built-in zero calibration system and protection against vapor and hydrocarbon contamination help to keep the 704 operating continuously and accurately.

the loading dock of a factory or warehouse. Trucks parked with their engines idling can cause CO problems which may not be noticed until it is too late. Forklift trucks can also contribute to the problem. The CO alarm makes sure an early warning is received.

Many underground garages install MSA CO alarms at key points and connect them to ventilator fan controls. The fans are started automatically when CO reaches a preset level, and shut off at a safe lower level. This not only saves on electric power, but also makes fan motors last longer.

Compressed air supply guarded against CO.

More and more CO alarms are being sold to industrial and government facilities to monitor compressed air used for breathing purposes. For example, NAVRAC Instruction 11300.24A requires installation of CO alarms for safe operation of the oil-lubricated compressors used to supply compressed air at Navy and Coast Guard locations. And MSA's CO alarm is the recommended detection device.

When compressors run hot due to excessive friction or after long periods of use, the lubricant may undergo partial combustion releasing carbon mon-

oxide in the supply air. To avoid fatalities and serious injuries, the alarm setting for the Model 704 should not exceed 50 ppm on the 0-100 ppm full-scale range.

Whether your compressed air is being used to fill air cylinders for self-contained breathing apparatus or to supply air-line respirators, check on the ease and accuracy of monitoring that air with the new 704 CO Alarm.

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2. Total plant area (square feet) which must be protected against CO.
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4. Present methods of detecting and measuring CO content.
5. Other pertinent details.

With this data, MSA engineers can help you with the correct CO alarm and detecting instruments. Please write MSA Instrument Division, 600 Penn Center Blvd., Pittsburgh, Pa. 15235, USA.

Make sure / check MSA

Environmental Science & Technology

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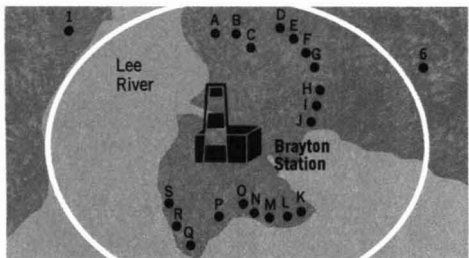
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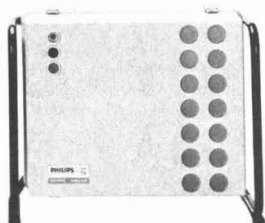
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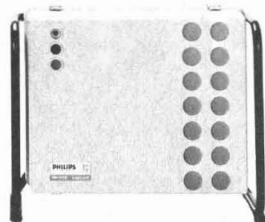
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On more than one occasion I have been asked to say what an environmentalist is, and I have found the request difficult to oblige. Just who are the "true environmentalists"?

The term "environmentalist" is often loosely applied to a wide range of persons with quite different goals, interests, and motivations. Some are ordinary citizens wanting improvement in the visible aspects of planetary nest fouling: dirty water and air, noise, litter, and crowding. Others, more recently anointed with the environmentalist label, are professionals in pursuit of basic scientific understanding of planetary processes. Still others are measuring or establishing social trends and mechanisms or are providing sustenance and satisfaction of perceived social needs.

Collectively, these activities have become a major political force for social reform. Approximately 3000 organizations, devoted to pollution abatement, scenic and wildlife conservation, and the preservation of the human race, have been identified. The dozen largest have a membership exceeding four million individuals and a combined budget in excess of \$48 million.

Who among these four million people are the "true environmentalists"? Most of the people in this melange share a belief that things are going awry with modern society and are vaguely anxious for some kind of reform. Many feel that the problems can be solved with greater clean-up efforts, and they seek a more substantial social commitment to this end. They believe that man has faced problems before, that he is resourceful by nature, and that he can, through the application of technology, make adjustments to remedy environmental problems.

I submit, however, that the true environmentalist differs from the others in one major respect; he believes that mankind is at a *unique* point in human experience. "Unique" is one of those adjectives that has no comparative forms. It is properly used to describe an event that has *never happened before*, and it is the recognition of that fact which distinguishes the true environmentalist from the hangers-on. The numbers of people, their collective life styles, and the potential of modern technology for irreversible effects persuades them that no major or minor application of clean-up, fix-up technology will solve the problems they perceive. Rather, what is needed is not only the adherence to altruism shared by all conservationists but, along with it, a willingness to undertake a basic revision of human values.



LETTERS

Dear Sir: The feature article titled "Determination of TOC in Waters" by Mr. Kehoe of Beckman Instruments (*ES&T*, February 1977, p 137) is interesting from an historical point of view. The classic technique of Van Hall et al., first described in 1963, certainly has been widely used since commercialization by Beckman Instruments around 1965. However, this is the only technique mentioned.

An article that is described in the table of contents as "All about TOC Analysis" is hardly complete without mention of more recently developed techniques for this determination. For example, the reductive method utilizing conversion of organic carbon to methane followed by flame ionization detection was commercialized by Dohrmann in 1972 and has been referenced in the *Federal Register*, Vol. 38, No. 199, Part II, October 16, 1973, as an applicable method for NPDES permit reporting.

Persulfate oxidation, followed by infrared detection, is the basis of an instrument manufactured by Oceanography International and is used by the Environmental Protection Agency (EPA).

Furthermore, a newer technique utilizing ultraviolet-promoted oxidation was not discussed, although reference to the work of Goulden and Brooksbank was listed for "additional reading." As a matter of fact, a variation of this method, using an acidic persulfate reagent, has also been commercialized by Dohrmann, and is currently used by the EPA Water Supply Branch as a method for both purgeable and non-purgeable organics in drinking water. The method is capable of detection at the 10-part-per-billion level, and does not share the problems alluded to by Mr. Kehoe in his discussion of TOC in potable water.

Leon E. Hiam

Envirotech Dohrmann
Santa Clara, Calif. 95050

Automobiles everywhere

Dear Sir: As a 7-y subscriber to *ES&T* not engaged in the chemical field, I have placed great value on your magazine as an information source on environmental matters. However, after reading your astonishingly biased editorial and box, "Some myths about automobiles," (January 1977), I am reluctantly forced to reexamine that faith.

The feature article by Mr. Iacocca was itself unsurprising and unremarkable. For the most part he limited the discussion to emission control and safety devices. His arguments were valid, though certainly debatable, within that very limited context. He made one point, though, which should have set off your editorial alarm bells. This

was that new car sales are expected to double in the next 23 years. The economic, environmental, and social impacts of such a continued expansion would be enormous. After 50 years of road building, urban streets and highways are still nearly saturated.

Cities with 25-60% of their land area already devoted to the automobile would be required to further decimate themselves with continuing massive road building. These same cities are even now experiencing difficulty in financing just the maintenance of existing streets. On top of this, gasoline prices will skyrocket as world oil production peaks out. Even assuming that the auto companies will not be successful in eliminating the 1985 27.5 mpg requirement, his happy prediction is a formula for economic and environmental disaster.

The fact that the automobile supports one-sixth of our economy is a testimonial only to its size, not its worth. In a similar fashion, our welfare system has become large, influential, and self-perpetuating; yet almost to a person we cry for something better. If you observe past and present history you will see that automobile dominance is not a requirement for healthy economics or societies. Alternative employment, such as construction of public transit systems, could easily become the "mainstay."

The question of why the automobile dominates transportation is far more complex than what is stated. Mobility, free choice, and symbolism have certainly all played a part, but so have governmental policies, lack of free choice, coercion, monopolies, and subsidies.

You say people do not buy what they do not want. They also do not buy what is not available. It has been decades since the great bulk of Americans have had any real ground transit choice. A few buses or an ancient rail line are hardly attractive competition for millions of subsidized automobiles, parking lots, and roads.

The key element here is subsidy. Since you are in the mood for myths, try the one about the automobile paying its own way. Practically every public activity has intimate and largely unperceived auto subsidies (the impact on personal values you speak of). City-owned parking lots, court expenses, police activities, assessment districts, lost property taxes are but a few of the less obvious subsidies. My own extrapolations, which are supported by other studies (ref. 1), indicate that auto subsidies from city governments alone add up to \$4-8 billion yearly, coming largely from sales and property taxes. This is in addition to the coercive and self-perpetuating gasoline taxes, which can also be used only for roads.

A concept that is rapidly gaining popularity in California is Full Cost Pricing (ref.

7). In this concept all identifiable auto-related costs will be paid for from automobile user taxes such as gasoline and registration taxes, with a dollar-for-dollar reduction in sales and property taxes. Thus the public will receive significant relief from one of its most vexing problems, and at the same time the true dollar cost of automobile usage will become readily apparent.

There is also a vast body of institutional protection for the automobile. A glance at the various city ordinances and the makeup of public bodies will make this apparent. Organized or even conscious conspiracy need not be involved. The automobile has become so entwined with our economy and values that it is protected simply from individual self-interest. On that point we agree. But habits and promotions are not "needs."

When adequate alternative transit is available, it is used and it is successful. The demise of a number of free-enterprise trolley lines was caused, not by lack of profit or patronage, but from being bought out and ripped up by automobile interests (ref. 2). On the other hand, the restoration of transit requires much more than just being "better." To catch up it requires large capital investments and favorable governmental regulations. In other words, it requires what the automobile has now.

Obviously, I cannot do justice to my argument in so short a space. What I hope to have done is present a sufficient number of considerations to demonstrate the shallowness of your comments. Such biases should never be allowed in a first-class technical magazine. Hopefully you will be inspired to publish a thorough and more even-handed article on the subject.

Robert L. Williams

Director, Modern Transit Society
San Jose, Calif. 95150

References

- 1) "State Transportation Plan," California State Transportation Board, September 1976.
- 2) Leonard Arrow, "Derailing America-GM's mark of excellence," *Environmental Action*, Vol. 5, No. 21, March 16, 1974.

Comment

Our editorial statement was to the effect that the automobile is deeply important in the American value system and that Congress did not intend to alter that valuation with the passage of the Clean Air Act. It has a more modest goal, namely, to clean up present exhaust emissions.

One may indeed argue that we need additional and more stringent regulation, or that present market place judgments reflect the lack of free choice, or deplore that in the human condition habits tend to become confused with needs. We agree, but that was not the point of the editorial.

Russell F. Christman

Editor, *ES&T*

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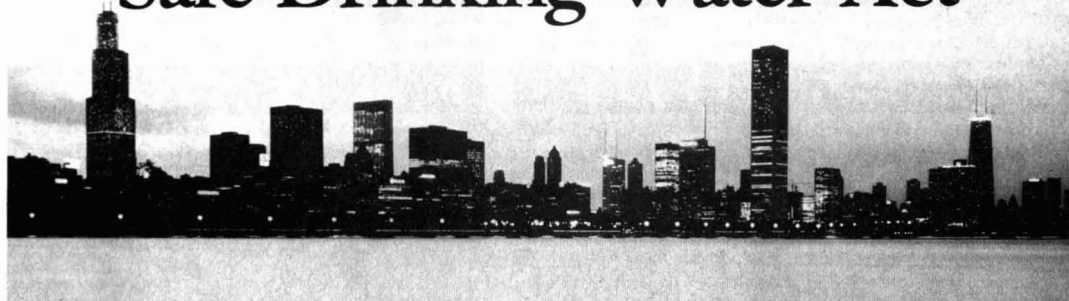
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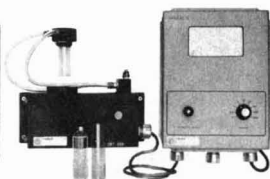
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CURRENTS

INTERNATIONAL

Monitoring makes up 9% and 12% of the proposed UNEP budget for 1978 and 1979, respectively. According to the planning document of the United Nations Environment Program, the Governing Council at its fifth meeting (Nairobi, Kenya) last month planned \$2.8 million out of a total of \$31.6 million in 1978 and \$3.5 million out of a total of \$30 million for 1979 for the Global Environmental Monitoring System. GEMS is the monitoring part of Earthwatch (*ES&T*, March 1976, p 230). Other major funding groupings include human settlements and human health; terrestrial ecosystems; environment and development; and oceans.

WASHINGTON

In his maiden speech, EPA administrator Douglas M. Costle pledged that "EPA will be persistent and consistent," but vigorous in carrying out its mandate. As far as jobs and the economy are concerned, Costle said that environmental laws have had only a minimal impact on the GNP and the CPI, and that the unemployment rate for 1977 is expected to be 0.5% lower than it would be without the required environmental expenditures. Citing a national health care bill of \$140 billion/y, Costle called for disease prevention through behavioral modification and environmental protection. The agency's deputy administrator, Barbara Blum, ordered a 30% cut in paperwork related to reporting requirements under EPA regulations. She convened an 8-member special task force to develop recommendations to achieve this goal.



EPA's Costle & Blum

Federal, state and local governments spent nearly \$8.9 billion on pollution controls during fiscal 1975, according

to the Dept. of Commerce's Bureau of the Census. The total is almost \$2 billion more than that spent in fiscal 1974. Of this total, nearly \$6.3 billion was spent for water quality controls; \$2.3 billion for solid waste management; \$306 million for air quality controls and \$118 million for other environmental quality controls. The Federal government spent \$2.9 billion, state government expenditures increased to \$984 million, and local governments spent \$7.7 billion for environmental controls in fiscal 1975. Of the state expenditures, Ohio spent more than any other state—\$171 million—for pollution control during fiscal 1975; and North Dakota spent the least—\$532 000.

Does the Clean Air Act authorize EPA's policy of no significant deterioration in air quality in relatively clean-air areas? The Supreme Court agreed to hear arguments of utilities and industrial groups that the act does not give EPA this authority. However, this question may be nullified by a proposed amendment to the Clean Air Act currently before Congress. The amendment would provide for authorization for a nondegradation policy and for implementation of EPA regulations in this regard. The Supreme Court also accepted EPA's offer to rewrite traffic control program regulations that, as now written, ordered states to clean up automobile exhausts. In an action that vacated three separate appeals court decisions, the Supreme Court gave the EPA the chance to draw up constitutionally acceptable regulations to assure that provisions of the Clean Air Act are implemented.

The NSF has set aside nearly \$1 million to award to small businesses for research on: chemical hazards to humans and the environment; regulatory effects of chemical process industries production; and the consequences of new composite materials in use in industry. Up to 40 awards will be made to small companies as part of the National Science Foundation's Research Applied to National Needs program. If a submitted proposal shows promise for generating a new product or business, the NSF will offer additional funding, and the businessman will be allowed to retain title to all patents.

Hot water reservoirs may be located near major urban centers in the eastern U.S., and these centers may be tapped for space heating or for low temperature heat for industrial processes. Under an Energy Research Development Administration contract, Virginia Polytechnic Institute scientists have preliminary findings that indicate that geothermal energy sources are buried under or near Savannah, Ga.; Charleston, S.C.; Baltimore, Md.; Norfolk, Va.; and Jersey City, N.J. ERDA's solar energy budget was given a boost in the revised fiscal 1978 budget. Planned outlays were increased from \$235 million to \$250 million, and solar heating and cooling was given an additional \$45 million for demonstration projects. This latter amount will provide for 1300 additional residential and commercial demonstration units.

Under its environmental pollution program, the NBS racked up an impressive list of accomplishments this past fiscal year. Besides a new instrument for measuring very low levels of ozone in the troposphere, the National Bureau of Standards, together with NOAA, has found that chlorofluorocarbon molecules containing hydrogen are less likely to reach the stratosphere intact to reduce ozone concentrations there. NBS issued a series of standard reference materials suitable for the industrial analysis of beryllium, lead, and cadmium. NBS scientists have developed two laser-based instruments that can characterize the nature of air particles 1 μm or less in size, and have developed a noncontaminating device for retrieving water samples taken from great depths.

STATES

Connecticut and Oklahoma are the first states to assume enforcement of P.L. 93-523, the Safe Drinking Water Act of 1974. These states were the first to develop acceptable programs to regulate the quality of drinking water and, as such, will assume the responsibility of enforcing the national standards developed by the EPA. The acceptable state programs provide for: state drinking water standards at least as stringent as federal standards; laboratory certification programs; surveillance programs; procedures to review the design, construction or

modification of treatment facilities; enforcement programs; and record-keeping and reporting programs. Other states in Oklahoma's Region VI are expected to assume enforcement responsibility soon, according to John C. White, EPA Region VI administrator.

The Ohio EPA is surveying industries throughout the state to obtain data on SO₂ and hydrocarbon emissions. The SO₂ survey covers emission data for 1974 and 1976; the data will be used to develop state regulations for controlling SO₂ emissions rather than adopting federal regulations, which agency officials claim will cause high unemployment among coal workers. The state agency, using what they claim will be more realistic data, will develop SO₂ regulations designed to attain and maintain the naaqs for SO₂. The state's hydrocarbon survey will inventory emissions for the year 1975, and the collected data will be used to revise Ohio's SIP for oxidants; the current SIP was termed inadequate by the U.S. EPA. Ohio's EPA budget request of nearly \$25 million may be cut by \$2.5 million, an action Ned Williams, director of the agency, says will "dismantle this agency."



Ohio EPA's Williams

San Francisco's BART system received the ASCE's Pioneering Design and Construction Award, the first such award ever given by the American Society of Civil Engineers. The Bay Area Rapid Transit System, the first totally new mass transit system constructed in the U.S. in the last 50 years, was cited as a "trailbreaker in rail transit technology"; the award was based entirely on the civil engineering accomplishments of the project.

Washington's Dept. of Ecology recently completed its first recycling survey. Seventy-two of 221 recycling centers throughout the state reportedly handled 121 194 tons of material in 1976. The market value was \$7.7 million. Among the materials recycled were: 7814 tons of aluminum; 14 000 tons of container glass; 18 086 tons of newsprint and 12 521 tons of other paper; 18 669 tons of ferrous metals; and 3762 tons of nonferrous metals. The difference between manufacturing

items from virgin materials as opposed to recycled materials—the energy savings—was pegged at 701 million kilowatt hours, which would satisfy the electrical requirements of some 46 000 homes for one year. The recyclers estimated that they diverted 332 tons of waste/day from the solid waste stream.

Under N.J.'s new Spill Compensation and Control Law, the Dept. of Environmental Protection adopted initial regulations and a list of oil and hazardous substances that are subject to taxation under the law. Crude oil, petroleum products, substances listed as hazardous by the U.S. EPA, certain pesticides and, eventually, radioactive materials and liquefied natural gas are subject to a 1¢/bbl transfer tax between major facilities. This tax will be placed in a fund to clean up spills and to compensate owners of property damaged by spills. Remaining to be adopted are comprehensive spill prevention and cleanup regulations. Among the initial regulations adopted was one requiring the registration of spill cleanup companies.

AWARDS

Odum receives Tyler ecology award. The fourth annual award of \$150 000 offered by the Pepperdine University (Malibu, Calif.) was awarded to Dr. Eugene P. Odum of the University of Georgia by President Carter. The ideal person to receive this award would be one who has performed adequate research, practical or applied research, and dissemination of knowledge. Odum was awarded the prize for his educational contributions to basic and applied ecology. He authored the first textbook written for the beginning ecology student to take the holistic and synthetic approach—the approach that ecology is today—as opposed to the reductionist, descriptive approach that preceded it. The book is in its third edition and has been translated into nine languages.

MONITORING

Pollutant transformations in power plant stack emissions—for example, from SO₂ to sulfate—are under study by Battelle Pacific Northwest Laboratories (Richland, Wash.). Research aircraft will carry instrument to sample data from coal- and oil-fired plants in Ind., Mass., and Mich. The aim is to get a better "handle" on rates and amounts of SO₂-sulfate change, and of the fate of what sulfates are made. Enough data will be collected to develop a computer model of the actions of SO₂ and sulfate in the atmosphere, so that more meaningful emission standards might be developed

for sulfate, as well as SO₂. If these standards call for further SO₂ decreases, ways will be explored to minimize the economic impact on power generation.

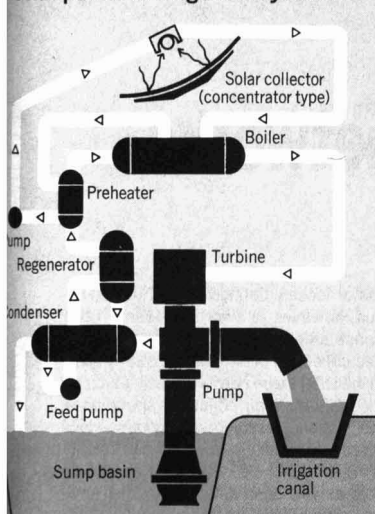
A thermographic scanner mounted aboard aircraft was used to survey heat loss from buildings in 26 Minnesota communities. The flights occurred from November 1976–March 1977. The project was the combined effort of the EPA, ERDA, and the Minn. Energy Agency. The scanner took infrared photographs that recorded heat loss from poorly insulated rooftops, under-insulated pipes, exposed industrial equipment, and other sources. These infrared photographs were compared with conventional shots of the same areas to identify heat loss from individual buildings and objects. Under Minnesota's Energy Outreach Program, the infrared photographs with interpretation will be made available to the public. The tripartite project team is developing a scanning "how-to" manual for use by other states and localities.

TECHNOLOGY

A wet combustion process has been patented by Dr. Donald F. Othmer. The process oxidizes wastes in sewage waters, wet garbage, and the like—thereby producing energy. The waste materials "ignite" in water at about 300 °F in a closed tank under pressure, when oxygen or air is injected. This patent, 4,017,421, issued April 12, 1977, improves efficiency and cuts capital expenditures by using heat-exchanging and batch-processing methods. As much heating value can be obtained as if the solid wastes were dry. The process has been licensed to a U.S. firm active in the pollution control field. Dr. Othmer is distinguished professor of chemical engineering at the Polytechnic Institute of New York, and a long-time ACS member.

The world's largest solar-powered irrigation system was dedicated at the Gila River Ranch, southwest of Phoenix, Ariz. The ranch is owned by Northwestern Mutual Life Insurance Co. (NML, Milwaukee, Wis.); the irrigation system was developed as a joint project of NML and Battelle Memorial Institute (Columbus, Ohio), and can pump up to 5.6 mgd of water during a June day of 9.5 h, for example. There are 550 ft² of parabolic tracking solar collectors into which water is pumped under pressure and heated. The water then vaporizes liquid Freon; Freon vapor runs a Rankine-cycle turbine that operates the irrigation pump. Pump size, which can be scaled up, is 50 hp.

Solar-powered irrigation system



Energy storage can be incorporated when desired.

Development of a new, cheaper method to remove sulfur, NO_x, and other pollutants from coal has won agreement by the governors of 13 Appalachian states to provide funds for initial stages, through the Appalachian Regional Commission. This method is known as the Sulf-X process, a proprietary development of Pittsburgh Environmental & Energy Systems, Inc. (PENNSYS). It uses a liquid sulfide slurry that is vaporized and mixed with flue gases from coal, lignite, or oil to remove SO_x and NO_x. Clean gases pass off; sulfur and reusable iron oxides are by-products. Pyrites can provide the sulfides needed, and acid mine drainage or steel "pickle liquors" work well in the system. Ash is also recovered. PENNSYS estimates that operating costs are \$1.27 plus 30¢/t royalty. Westinghouse will participate in the development project.

Reclaiming water, returning solids to land, and recovering energy are the functions of the 36-mgd wastewater treatment plant at Albuquerque, N.Mex., where water is a "meticulously conserved asset," as Koppers Co., Inc. (Pittsburgh, Pa.) expressed it. Reclaimed water goes to the Rio Grande, and is used for irrigation. Solids condition soil in Albuquerque's parks and public golf courses. Anaerobically-made methane helps to generate power, thus reducing other energy consumption. Special coatings made by Koppers allow plant equipment to withstand severe chemical attack and corrosive effects of polluted water, as well as temperatures that can range

from -17 to +105 °F. The plant uses Archimedes screw pumps and elevated aeration tanks, and is to expand to 47 mgd by 1983.

Over 99% of BOD can be removed from industrial effluents highly loaded with organic matter, especially those from food industries. For example, at a pickled cabbage factory with an average BOD of 36 000 mg/L (peak, 70 000 mg/L), the MULTOX process, developed by Menzel Abwassertechnik (Stuttgart, W. Germany), reduces this BOD to below 24 mg/L at the outfall. According to the company, the special multi-stage activated sludge process combines multi-stage advantages with economy of single-stage plants. Among advantages listed are high space loadings with lower activity volumes; buffering of pH and toxic surges; less excess sludge; and optimization of oxygen use in relation to actual oxygen demand.

INDUSTRY

An electric utility official wants a workable energy-environmental plan. Edison Electric Institute president Don Crawford said that a utility can either install scrubbers or burn low-sulfur coal to comply with existing law. In his view, a probably low minimum of \$100 per kilowatt as the cost of installing scrubbers on new plants plus the fossil fuel cost may add up to \$12.8 billion of scarce capital in nine years. Crawford said, "The ultimate answer to the problem of sulfur removal may well be found in processes to remove sulfur before combustion or in the combustion process. An expenditure of billions of dollars on scrubbers, particularly if not necessary to attain clean air standards, will be a major disincentive to developing better processes."



IGCI pres. Wright

IGCI reports 1976 orders down from the previous year. New orders for industrial air pollution control apparatus in the U.S. hit \$294.8 million, down from \$357.9 million the previous year. Industrial Gas Cleaning Institute president Robert J. Wright says these figures represent orders of the 37 member companies of the IGCI (*ES&T*, September 1976, p 866) and are bare

apparatus, net f.o.b. shop costs. At the same time, fabric filter and wet scrubber orders were higher in 1976 than 1975, but orders for electrostatic precipitators were less than 55% of the total for 1975. Combined orders for Canada plus the U.S. hit \$357.8 million, down from \$374.5 million, down from 1975 figures.

For the first large-scale experimental sludge gasification plant, Jacobs Engineering Co. (Santa Monica, Calif.) is performing engineering and construction management. The \$2.8 million facility is being built for Waste Management, Inc., and is to convert solid wastes and sewage sludge to clean-burning methane gas at Pompano Beach, Fla. The plant is to process 100 tpd of solid waste, and produce about 3000 ft³ from every ton of refuse processed. The facility, funded by ERDA, will provide base data on quality/quantity of gas, and optimum design and operation parameters for future commercial application of waste-methane conversion. According to Jacobs, a 1000-tpd plant would provide gas needs for 10 000 homes, and reduce solid waste volume by about 70%.

\$30 million of contingent liability insurances for nuclear reactors becomes available August 1, according to the Nuclear Energy Liability Property Insurance Association (NEL-PIA). Each power reactor will be assessed a retrospective premium up to a maximum of \$5 million/reactor by the nuclear insurance pools if a nuclear accident at any reactor results in liability losses exceeding the primary protection of \$140 million. The \$30 million would be a buffer if one or more operators cannot meet their assessment obligations at the time of loss. The insurance pools would seek repayment of any defaults from these operators at a later date.

The steel industry is prepared to meet its share of the national cleanup bill, now estimated at "easily" \$500 billion by the early 1980's, according to the American Iron and Steel Institute (AISI, Washington, D.C.). To do so, however, steelmakers must raise \$12-14 billion/y by 1983 in the face of "enormous capital formation problems" made even more complex by the energy factor. On that subject, Harry Thomas, chairman of AISI's Committee on Energy, expressed support for efforts to convert the industry from other fuels to coal. He told a Senate committee, however, that the January 1, 1979 deadline is "unrealistic," and proposed an 8-year conversion period instead. He also cited numerous cases in which coal use is simply not feasible.

Building air monitoring networks

One new aspect on the environmental scene is air monitoring networks. Before the environmental decade of the 1970's is over more than 100 networks plus an additional 200-300 monitoring stations worldwide will be operational. More data are being collected on air quality than ever

before. They form a record on which air pollution cleanup can be documented. They also provide an instantaneous reporting when potentially dangerous levels of pollutants impact on human health.

Monitoring instruments, minicomputers, and engineering construction form networks that are a base for environmental protection. The need for such networks has become increasingly obvious to a growing number of environmental watchers. These observers point out that such systems:

- keep a watch on pollutants to ensure that air quality levels are not exceeded and that the public health is protected
- accumulate an uncontested log of airborne air quality on a global basis
- document the movement of pollutants across national boundaries, particularly in highly industrialized western Europe.

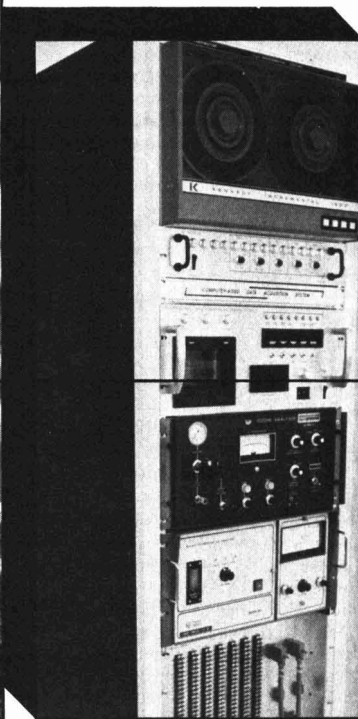
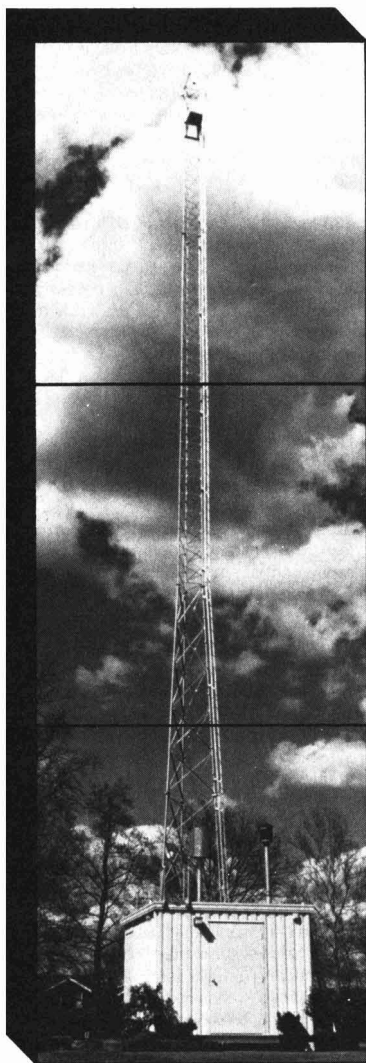
But network building has come to be a

rather loosely defined term. The end result, however, is always the same—the construction of a system for the systematic collection of ambient air quality data. In the U.S., these networks keep watch on the half-dozen air pollutants specified in the national ambient air quality standards—SO₂, total suspended particulates (TSP), oxidants, CO, and NO₂. No standard has, as yet, been established for hydrocarbons. Elsewhere in the world, a first concern is with SO₂ and TSP only. Japan is monitoring most of our naaqs pollutants.

In the business

Firms in the three different areas of network building bring their individual capabilities to bear on the demand for a warning of harmful concentrations of air pollutants. Quite a number of companies, both in the U.S. and western Europe, have devoted a portion of their business operation to such networks and stations. Many are instrument manufacturing companies. They can and do provide monitoring instruments for use in such networks and stations. In addition, other companies handle the computer data processing and reporting elements of the business. Some companies handle two aspects of the network building. But, in fact, only a few companies provide all three services.

Three basics. Monitoring and meteorological instruments plus computer data processing give the director at the control center data on the buildup of pollutants



ES&T's Stan Miller finds that such systems simply did not exist before the environmental decade, and that these lone sentinels ensure corrective action when excessive emissions burden our breathing space

Companies such as Philips (the Netherlands) and Environmental Research & Technology, Radian, and Rockwell (U.S.), for example, have built, can, and will build complete networks. At the same time, there are many other companies that provide only instruments (*ES&T*, November 1973, p 1011), including Bendix, Meloy Labs, Monitor Labs; Hartman and Brown in Germany; and Seres in France. In the area of minicomputers and data processing equipment there are ITT, Radian Corp., and Rockwell (U.S.), and Siemens (Germany), among others.

Monitoring networks represent a considerable economic investment. But it must be remembered that these continuous monitoring networks, on which the alert or warning system is based, do not replace permanent environmental controls. But this alert system is necessary as a safety measure, protective of human health, against unfavorable meteorological buildup of air pollutants.

Network builders certainly differ; not two are exactly alike. In the U.S., ERT, Radian, and Rockwell International (part of Atomics International, Inc.) are network builders. They provide that third element of coordination. In a sense they act as prime contractors. In turn, each might subcontract for the individual segments—the instrument package or the data collection and reduction package. ERT also has an international subsidiary presently developing a monitoring system in Saudi Arabia.

In addition to the air monitoring activities of these companies, some of these, plus others, are concerned with water monitoring networks. For example, Radian Corp. is utilizing such systems for hydrologic baseline studies in conjunction with coal mine environmental studies. ERT has a water monitoring network operational in Florida, and another planned in Arkansas. These networks are in their infancy today, as were the air networks at the beginning of the environmental decade.

U.S. monitoring

At the end of the fiscal year 1976 resources, state and local air pollution control agencies, including those not receiving Federal support, totaled approximately 7000 man-years and \$157 million. Robert Neligan, director of monitoring and

data analysis division of the EPA (Research Triangle Park), said that on an annual basis about \$31 million went for ambient air monitoring and \$18 million for source monitoring.

The breakdown in ambient air monitoring includes \$24 million for the total operational cost including equipment procurement, \$4.5 million for special purpose monitoring, and \$3 million for quality assurance. About 1100 man-years of state and local personnel went into this air monitoring activity. The breakdown for the source monitoring includes \$7 million for emissions inventory, \$8 million for source testing, and \$3 million for special studies. So in effect, out of the \$157 million for last year, \$49 million, went for monitoring activities.

In September 1975, EPA reviewed its air monitoring activities pursuant to the Clean Air Act to see what level of monitoring was being done under the state air implementation plans. What EPA found was that in 1975, for the first time, the total number of reporting stations was beginning to stabilize. The number of sites at which monitoring has been conducted during the period 1970–1975 was: TSP, 4060; SO₂, 2579; NO₂, 1726; oxidants, 509, and CO, 443. Most of these are integrating, not continuous, stations.

With a few exceptions—American Samoa, the District of Columbia, Nevada, Pennsylvania, and Virginia—all states were providing annual summaries of pollutant levels, as required under the Clean Air Act. All states submit the raw data to the EPA but not annual reports, which some may prepare on their own.

In the first half of last year, there were 111 air pollution episodes in a dozen states in a half-dozen air quality control regions, according to the latest EPA statistics. High oxidant/ozone levels were responsible for 91. Seventy-eight were recorded in California alone. The remaining episodes were scattered among excess levels of TSP, CO, SO₂, and TSP X SO₂.

In addition, the EPA at Research Triangle Park, N.C., has been designated as the processing point for worldwide data reporting under the GEMS activity of the United Nations Environment Program (*ES&T*, March 1976, p 230). There is planned expansion for the GEMS activity. EPA's David Shearer and Jack Thompson

reported that in this calendar year, 14–15 new monitoring stations will be activated. There will be more next year; and by 1981 it has been estimated that there will be 150–200 national monitoring stations as part of the UNEP's GEMS program.

These new monitoring stations for 1977 are outside the U.S., in third world nations. They will be set up in developing nations of Africa, Asia, and the Middle East. The instrument package for these sites consists of SO₂ bubblers and HiVol samplers, being provided by the Research Appliance Corp. (Gibsonia, Pa.) under a \$163 000 procurement contract let by the World Health Organization last fall.

Data from these stations, as well as data from the other 40 sites in 14 countries on the WHO map, are sent first to the WHO regional office, then to WHO headquarters (Geneva, Switzerland), where they are packaged quarterly and sent to the U.S. EPA at Research Triangle Park for insertion in the worldwide air quality data bank.

The EPA is faced with an awesome collection of information, not only that involved with state implementation plans but that of incoming data on worldwide air pollutants. Last November, Computer Network Corp. (Washington, D.C.) was awarded a \$20 million contract from the EPA for its agency-wide data processing requirements. Over the next four years the contract will total \$23 million.

The contract requirements call for a dedicated IBM 370-168 computer system with 16 billion bytes of high-speed data storage to support one of the largest data bases within the Federal Government. This data base storage will meet EPA requirements in a number of areas, including trends and monitoring.

Business activity

In the U.S., there are three major network builders. One has offices on the East, West, and Gulf coasts, another in the south, and a third in the West. Their experiences show the present activity of network building.

Environmental Research & Technology (Concord, Mass.) provides the three elements of network building. ERT's system of Air Monitoring, Analysis, and Prediction (AIRMAP[®]) was designed for the management of individual air quality monitoring networks. It can comprise any

ห้องสมุด กรมวิทยาศาสตร์

number of monitoring stations that may be at remote locations. ERT provides total environmental consulting services to both industry and government.

ERT's first small network was established in December 1971; now, there are 45-50 networks in operation. AIRMAP is the largest privately owned air quality monitoring network in the world. It includes nearly 260 field observation sites measuring more than 1000 parameters (742 in real time), all under centralized computer control. The cost of the instruments alone is in excess of \$4 million. The data gathered from the network are processed and monitored at Chicago AIRMAP Central and at Concord AIRMAP Central, located at ERT corporate headquarters.

AIRMAP provides to industrial subscribers real-time information about air quality in the vicinity of their manufacturing plants. It includes forecasting of pollutant levels and provides its industry and government users with predictions of pollutant levels for the next 30 hours of plant operation, at 3-h intervals. For example, AIRMAP assesses the environmental impact of operation and identifies the most appropriate fuel management strategy for operating under different meteorological conditions. Actual or potential users include electric power utilities, chemical plants, petroleum refineries, paper and mining operations.

ERT has been a leader in the design and operation of cost-effective Dynamic Emission Control (DEC) systems, often called Supplementary Control Systems (SCS). But as yet, these systems are not acceptable to the EPA. The purpose of such systems is to achieve and maintain the air quality levels specified in the national ambient air quality standards. DEC appears to be one of the few economically feasible ways to maintain air quality standards while still conserving scarce low-sulfur oil and coal.

The field monitoring stations (shelters) of AIRMAP measure ambient levels of SO₂, NO, CO, and CO₂, as well as TSP. Wind speed and direction and temperature and precipitation are monitored with

meteorological instrumentation, often mounted on towers located outside the shelters.

The AIRMAP computer centrals collect and process field monitoring data from all of the instruments in the system and processes it into useful forms of output, such as plant equipment control settings. Trained forecasters combine this information with National Weather Service data and the output of ERT's air quality forecasting models to provide its predictions of pollutant levels.

ERT instruments, its System 5000 stack gas analyzer, and the Model 7000 instrument control unit were created by the company for use in AIRMAP. Both are available for outside purchase now. The stack gas analyzer provides continuous flue gas monitoring of stationary source emissions for SO₂, NO, CO, and CO₂. The instrument control unit is a flexible microcomputer that can be configured to perform a wide variety of instrument control functions and easily tailored to specific customer applications.

Though nationwide in scope, **Radian Corp.** (Austin, Tex.) has concentrated its monitoring activities in the South and the West.

Radian has operated air monitoring systems in a broad range of industrial and geographical settings (nine states). The company claims to have conducted more than 75 system-years of air quality monitoring totalling in excess of \$6 million.

Radian does not manufacture meteorological or air quality instrumentation. But it does design and manufacture a piece of equipment that serves as a data acquisition system as well as a controller for the air monitoring system. This data equipment system—a microprocessor-based, programmable minicomputer—allows software changes in the field. Such data acquisition systems, for example, are included in a recent sale of 15 systems to Pennsylvania. Using the technology of the microprocessor to produce the data acquisition system has greatly reduced the cost, while increasing the capability of the monitoring network.

Radian maintains an on-going laboratory for the testing and evaluation of air quality instrumentation. Because many of Radian's networks include comprehensive service contracts, a knowledge of maintenance and operation requirements for the instruments is critical to the design of the most cost-effective approach. Through this testing process Radian has selected instruments from Meloy Laboratories, Monitor Labs, Phillips, Teco, Bendix, and Dasibi, with others still under evaluation.

At the same time, a meteorological equipment test facility is part of this testing laboratory. This lab provides design information for the field equipment and permits the evaluation of vendor hardware. For example, Radian has utilized meteorological equipment from MRI,

R. M. Young, Climet, Weather Measure, Climatronics, and Texas Electronics.

Radian monitoring services and systems are available on short- and long-term lease, and by direct sales. These leases can be for equipment only or a complete turn-key service. The system reports the information either through magnetic tapes produced on site or through teleprocessing communication networks tied through the Radian STAR system, a central computer facility (Austin, Tex.), linked to the field with telephone communications.

In the West, **Rockwell International** is the label. Last November, a \$1.26 million quality assurance program contract for 26 air monitoring laboratories throughout the western U.S. was awarded to the Air Monitoring Center (AMC) of the Atomic International Division of Rockwell International (Canoga Park, Calif.).

Under this 5-y contract with the EPA, the program is for state and local agencies monitoring air quality around present and proposed energy development projects in Arizona, Colorado, Montana, Nevada, New Mexico, North Dakota, South Dakota, Utah, and Wyoming. The AMC will provide on-site inspection and audits to assess the quality of data being obtained by the laboratories, and technical assistance to improve quality.

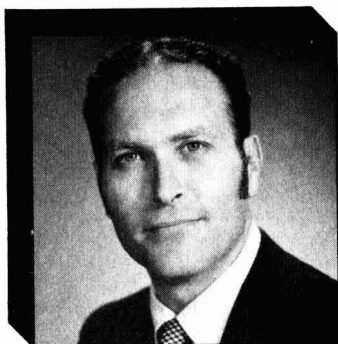
AMC has also designed, constructed, and operated some of this nation's most extensive air quality networks. It is another pioneer in the field, and was the prime contractor for the EPA nationwide Community Health Air Monitoring Program (CHAMP). Built in 1973, the CHAMP effort was one of the first to apply strict comprehensive quality assurance procedures to the systems in a large air monitoring network and to the resulting data. (Earlier there was the CAMP—Community Air Monitoring Program—of NAPCA, the first monitoring network in the U.S.)

The CHAMP network of 23 remote stations in five states—southern California, Utah, Alabama, New York, and North Carolina—provided valid air quality monitoring that might then be correlated with the health of the population in those areas. Pollutants measured were SO₂, NO_x, ozone, hydrocarbons, TSP, and PAN (peroxyacetyl nitrate), plus five aerometric components—wind speed, wind direction, barometric pressure, relative humidity,

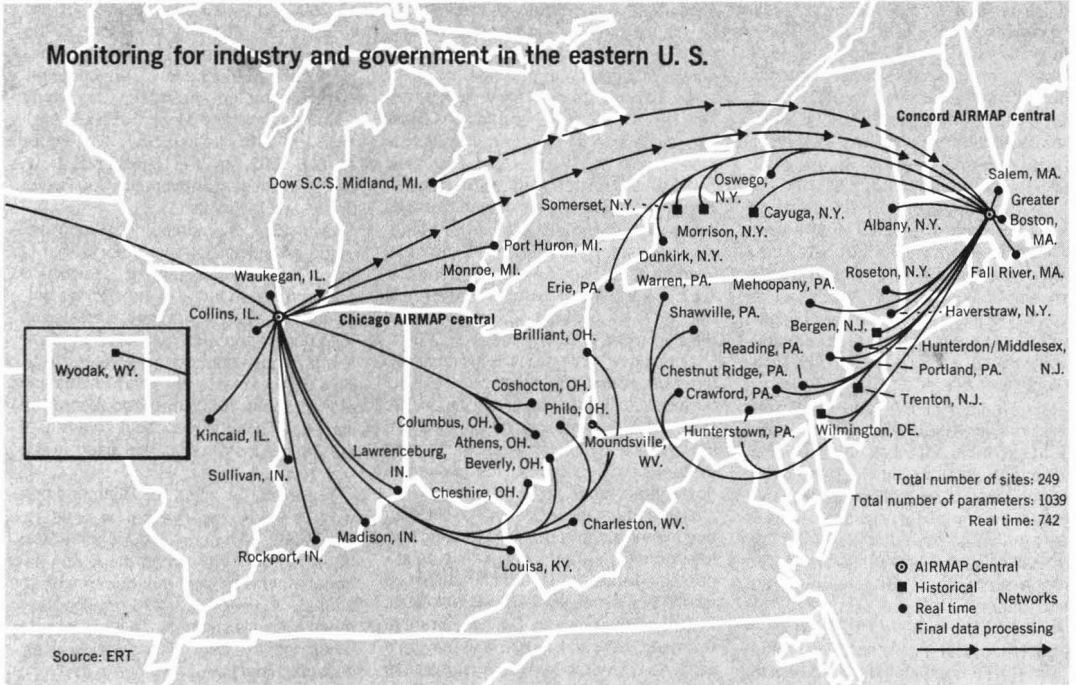
As the prime contractor for the EPA's RAMS/RAPS Program, Rockwell Air Monitoring Center became involved in the entire spectrum of design, development, fabrication, assembly, station siting, test, and long-term operations and maintenance of a total regional air monitoring system. RAMS, Regional Air Monitoring System, built and operated for the EPA by the AMC, is one of the most sophisticated air quality monitoring networks ever undertaken. It is the major fixed-base data acquisition portion of the larger program known as RAPS, Regional Air Pollution Study (ES&T, July 1973, p 598).

ERT president Gaut

"Services for industry & government"



Monitoring for industry and government in the eastern U. S.



The 25-station network is located in both the Missouri and Illinois portion of the greater St. Louis area. The central purpose of the RAPS is to produce for a single urban area enough information on all processes that determine the concentrations of air pollutants so that they can be described in a system of mathematical models. This objective led directly to the requirement that there be generated an extensive base of air quality measurements against which calculated values may be compared.

The 25 remote monitoring stations are connected via four telephone lines to a central computer facility located in Creve Coeur, Mo. Each station contains analytical equipment to measure ozone (O_3), oxides of nitrogen ($NO-NO_2-NO_x$), hydrocarbons and carbon monoxide ($CH_4-THC-CO$), total sulfur, hydrogen sulfide and sulfur dioxide ($TS-H_2S-SO_2$), particulates, and relevant meteorological conditions.

A minicomputer in each station provides for data averaging and status information with real-time data available at the central facility every minute. Since each station is designed for unattended operation, significant features include the capabilities of automatic instrument range change, automatic calibration, automatic zero and span, and computer validation of the data gathered.

The world experience

As its contribution to GEMS, the World Health Organization (WHO) selected areas

in 14 countries where air quality monitoring data have been collected for the years 1973-1974. Only SO_2 and TSP were measured; different methods were used in each country. The published results became available last year. Data for 1975 will be published mid-1977, and data for 1976 by the end of this year.

In a major city in each of the 14 countries—St. Louis for the U.S.—three sampling locations were identified:

- an industrial area where manufacturing concerns, utilities, and granaries are located
- a commercial area where shops and shopping centers are located
- a residential area where there are no dominating stationary industrial or commercial sources of air pollution.

The WHO air quality monitoring project is being expanded both in terms of number of participating countries and the number of sites from which air quality data will be collected. Within the U.S. alone, six additional cities are being included under GEMS. This project provides an input to GEMS. In the U.S. it is managed under EPA's "WHO Collaborating Center on Environmental Pollution Control"; which is headquartered in Washington, D.C. The data processing is done at Research Triangle Park in N. C.

During 1975, an interlaboratory comparison for SO_2 , using the West-Gaeke method, was performed. Ten laboratories participated, and the published results are expected this year. At this stage of data collection no effort was made to select

any particular method for use by all participating laboratories.

As was noted by an interagency working group on monitoring for the development of GEMS, "One requirement . . . is common to all; the results of measurements or observations have to be comparable even when obtained by different operators and through different methods. The need, in other words, is to ensure, by the judicious selection, an intercalibration of methods and, by the determination of reference methods, that even without aiming at unnecessary analytical perfection, the results are not affected by major systematic errors or attributable to the observer or to other factors."

It is envisaged that the number of methods will gradually be reduced, and ultimately only those methods recommended in *Selected Methods of Measuring Air Quality*, (Geneva, WHO, 1976, WHO Offset Publication No. 24) will be retained. (In the U.S., of course, the EPA publishes its reference methods for air quality monitoring in the *Federal Register*.)

Meanwhile, an OECD report points out that unacceptable levels of air pollution may be 10 or more times the annual average. This overburden may last for a few hours or a few days. Prepared by a group of national rapporteurs from six countries—Canada, France, Germany, Italy, Japan, and the Netherlands—this report of the Organization for Economic Cooperation and Development notes that it is usually not economically feasible to

establish permanent controls on the basis of the worst meteorological condition. Obviously, the introduction of supplementary control actions, when required, offers a more cost-effective solution to the control of infrequent episode situations. But such control actions are difficult to enforce and manage in an urban multi-source area.

Three areas were reported in each of the six countries. The OECD areas are not to be confused with the WHO areas, since they do not constitute a network in the sense of GEMS. The OECD areas include a heavily industrialized area, an individual metropolitan area, and an area with relatively small population but specific topographic features.

The problem of SO₂ and particulate emissions are similar in all six countries, but the sources are widely different. For example, in northern Ontario, Canada, the Sudbury and Happy Valley are in the vicinity of the two largest nickel smelters in the world. Each smelter uses the pyrometallurgical process of treating sulfide ores; most of the SO₂ is released to the atmosphere.

In Italy, the urban area of Milan is the largest industrial and trade center in the country, with a population of 2.2 million. The meteorological conditions there are characterized by low wind speeds. On about 60% of the days in a year, there is no wind and only 2-3% of the time are there winds that exceed 10 m/s. In the territory of the Province of Milan, there are frequent thermal inversions, which often last several days, or even weeks, particularly in the period from October to March (ES&T, November 1976, p 1092).

What's an alert?

An alert system in combination with the application of specific temporary control measures offer the only means possible for avoiding unacceptably high pollutant concentrations. The essential components of the alert system are a real-time monitoring system and a reliable method for short-period meteorological forecasts. Together these components predict when exceptional air pollution situations might

arise. Good meteorological data alone can be used to provide an alert. An alert system is effective if it brings about a temporary reduction of emissions.

An alert level reflects the relative severity of air pollution concentrations under poor dispersion conditions. It also reflects the extent to which corrective action must be taken to bring concentrations down to acceptable levels. In the case of high SO₂ emissions, the specific types of abatement measures would include fuel switching. In case of high CO concentrations, restraints of motor vehicles may have to be imposed. Such restraints are difficult, at best, to enforce.

Specific regulations in the six countries differ but have been developed in all six for alerts. In France, Italy, and Japan, the local authority is responsible for the alert. In Canada and the Netherlands, the alert system is delegated to the provincial government level.

If and when an alert is called, a reduction in emissions is required to bring pollutant concentration levels within an acceptable range. It may be accomplished when compliance is mandated by law, as it is, for example, in Canada, France, Germany, Italy, and Japan. Or it may be a partly voluntary program such as the case for the Rijnmond area in the Netherlands.

The Netherlands real-time monitoring is the most comprehensive network in Europe. In effect, the Rijnmond authority is the only one in Europe that has developed an alert system (ES&T, May 1977, p 450). An alert is followed by measures taken by the industry to reduce all emissions on a temporary basis. It is important to note that this cooperation with industry takes place voluntarily. But in extreme cases a forced emission reduction can be imposed upon the industry based on the law. So far, this has not happened.

The success of any control action in preventing an episode is largely dependent on the degree of precision attached to the forecasting method. This point cannot be underestimated. In the Rijnmond area, industry requires a high degree of reliability in short-term forecasts.

On alert levels, in several countries, meteorologists are consulted regarding the persistence of the weather situation that is causing the pollutant accumulation. The specification of persistence associated with different alert levels range from six hours in Ontario and 12 hours in Montreal to 48 hours in West Germany.

Foreign business activity

Philips, the fifth largest company in western Europe, provides all three elements for network building. A leader in the field, Philips (the Netherlands) makes monitoring instruments and minicomputers for data processing and manipulation, and can put networks together.

Worldwide, Philips employs about

40 000 people in 70 countries of the world; about 10% of these are at the corporate headquarters and manufacturing facility in Eindhoven. This company has assembled networks in many countries including Mexico (ES&T, April 1976, p 316), Italy (ES&T, November 1976, p 1092), and the Netherlands. Now, Philips is building networks in Sao Paulo, Brazil, and in Finland.

Until 1972, the company had concentrated on monitoring instruments, but in that year its management decided to concentrate on turn-key monitoring networks. In January 1974, Philips created its PPM department (Philips Pollution Monitoring), whose marketing manager is A.B. Bok. By the end of last year, Philips had placed about 3000 of its monitoring instruments in the world; about 700-800 of the Philips instruments are used in the U.S. today.

For example, when the Rijnmond network became operational it used 31 Philips SO₂ monitors (ES&T, Oct 1973, p 896). In May 1973, when the Dutch national monitoring network became operational, it used 250-270 Philips SO₂ monitoring instruments. Divided into 11 provinces, this network has nine regional networks, the three provinces in the North being combined into one region.

Philips has installed many networks in many parts of the world. The company has sold more networks in Italy than in any other country. The tally on PPM networks include: Austria (15), Australia (1), Canada (4), Czechoslovakia (1), Finland (1), Holland (12), Hungary (1), Italy (28), Luxembourg (1), Mexico City (1), Poland (1), Roumania (1), Sweden (3), and Switzerland (2). Mexico City, Philips first large network outside the Netherlands, has 20 fixed-monitoring stations, a central computer, and two mobile monitoring vans, all costing \$1.5 million. Last year, NO, NO₂, O₃, and CO have been integrated into this network. The NO, NO₂, and O₃ instruments were purchased from Bendix.

J.W. Delwel, systems sales manager for the PPM, explains that the order for the Brazilian network came in August 1976. This network will cost \$6.5 million; it involves 25 fixed stations and four mobile stations. A new aspect of the Brazilian network involves the use of an acoustically tuned radar to measure the height of the inversion layer.

One must never assume that these instruments are put in place and that is the end of it. Newer instruments and techniques are constantly being refined by Philips, among others, and introduced in the newer networks. One of the newest aspects of the PPM activity is the simultaneous monitoring of stack emissions and ambient air quality.

Last fall, Philips was negotiating with a U.S. company on this approach. One of the first examples is a network to be constructed around a fertilizer plant, correlating real-time stack emissions with

Philips' Bok

"\$15-20 million commitment"



ambient air quality. Philips has also completed a \$110 000 study on the air and water monitoring needs for the whole of Canada.

Bok also pointed out that when Philips decided to enter the network field, the company committed a \$15–20 million investment to this venture in the air and water monitoring network business. Hopefully, it will pay off in 5 years. When Bok became marketing manager in 1974, he said the planning documents for the network business took five people two years to define that market. The PPM report was first presented to management in January 1976, and included 8 individual categories of monitoring activity.

The Dutch experience

The foresight and forbearance for the first monitoring of industrial emissions is attributed to Dr. Clarenburg, who now holds a parliamentary post in the Hague. He provided the leadership behind the Rijnmond network and was the first director when it became operational in 1969.

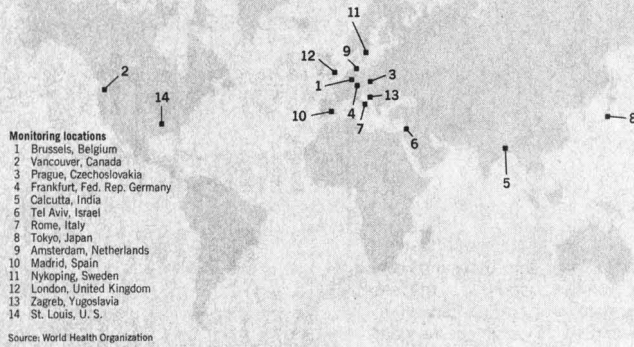
Today, the Rijnmond network covers 40 000 acres (an area 80 km X 30 km), where 1 million people live, work, and play. In other terms, the Rijnmond area is less than 2% of the Netherlands but contains more than 8% of the total Dutch population. It's a highly industrialized area that includes Rotterdam, the busiest port in the world.

P.A.R. Post van der Burg, the director of the Control Center for Rijnmond, pointed out that there are as many as 20 000 industrial installations in the area, including large oil refineries, chemical plants, and the like. He noted that various industrial growth periods had occurred in the area, including just before the war, after the war, the 1950's, 1960's, and 1970's, with a perceptible movement to the west. Today, the coastal area is being developed.

The director reminded *ES&T* that the Rijnmond Public Authority is the first example of a new form of local government organization in the Netherlands. Established by an act of Parliament on November 26, 1964, this authority unites 23 different municipalities in the area and coordinates their diverging interest.

The Dutch national air monitoring network was established in 1972 to protect the health of the public. This year, the 250 SO₂ station networks will be extended, with 100 stations for NO and NO₂, and 30 stations for CO and O₃. N.O. van Egmond, head of the data processing office at the Dutch National Institute of Health, the R.I.V. (Rijks Instituut voor de Volksgezondheid) explains that hourly data are sent from the nine regional networks to the central processor in Bilthoven. Each day, more than 5000 hourly values are recorded. He explains that the 24-h value is taken as a determination of the health effects.

WHO air monitoring project



Areas with monitoring networks and alert systems

Canada	Italy
Toronto	Milan
Hamilton	Venice
Windsor	
Sudbury	Japan
Montreal	Osaka
	Tokyo
	Chiba
Federal Republic of Germany	Yokohama-Kawasaki
Ruhr	Nagoya
Mannheim/	Kita-Kyusyu
Ludwigshafen	
Hessen	Netherlands
Ingolstadt	Rijnmond area
Munich	National system
Bavaria	in cooperation with
	the Royal Dutch
France	Meteorological
Rouen	Institute
Source: OECD	

In a report from the R.I.V., the data on yearly values for SO₂ are summarized. These data are presented in nine ranges of values from a low of 100 µg/m³ to a high of 250 µg/m³. Van Egmond estimated that the health effects level was exceeded about 2% of the time, or 7 days per year. There also might be three inversions each year, usually occurring during the months of September and October.

He also explained that the information from the monitoring network clearly shows that almost 50% of the SO₂ burden in the Netherlands is being imported from neighboring countries. And although human health effects appear minimal now, the daily values of SO₂ concentrations were in excess of the level at which epiphytes, an organisms used as a bio-

logical indicator in the air quality correlation work, are effected.

Prognosis

What is urgently needed in many more places of this globe are additional systems for predicting future concentrations of air contaminants several hours or days in advance, like those of the ERT AIRMAP in the U.S. and the Rijnmond network do today. Then control actions could be taken to avoid any buildup of pollutants. How? A so-called feed forward control would improve the network data and the alert system notification. This control would use mathematical modeling, taking into account all data collected by the central processing control, the synoptic weather data, and other materials.

Until the world reaches this totally reliable predictive stage, it cannot guarantee against future episodes of air pollution. Meanwhile, the incoming data will be useful in making future findings and correlations that seem impossible today.

Additional reading

Report on Use of Surveillance and Control Techniques for Air Pollution Alert Systems. Environment Directorate, Air Management Sector Group, Organization for Economic Co-Operation and Development, Paris, 1976.

Air Quality in Selected Urban Areas 1973–1974, GEMS: Global Environmental Monitoring System (WHO Offset Publication No. 30), World Health Organization, Geneva, 1976.

State Air Pollution Implementation Plan Progress Report, January 1 to June 30, 1976 (USEPA Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. 27711).

Chapter 13, Global Monitoring and Surveillance of Air Pollution, by Richard D. Cadle, In *Air Pollution*, Volume III, Measuring, Monitoring, and Surveillance of Air Pollution, edited by Arthur C. Stern, Academic Press, Inc.

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Monitoring fluorides at an aluminum smelter

At Alcoa, Tenn., the Aluminum Company of America operates a modern, center-worked, prebake, primary aluminum smelter. At this location, the company uses the latest technology for the Hall-Heroult smelting process. In this electrolytic process for the production of aluminum, the emission of gaseous fluoride is inevitable, resulting from the electrolyte—molten fluoride salts—in which the aluminum oxide is dissolved.

Obviously, uncontrolled fluoride emissions are an environmental concern. Excessive levels of fluoride can cause visible effects on vegetation and contaminate foraging cattle.

In the U.S., there are about 32 aluminum smelting operations. Alcoa has nine. All told, there are 12 primary producers including Reynolds, Kaiser, Anaconda, Intalco, Eastalco, and Conalco. But not only these aluminum processors are concerned with gaseous fluoride monitoring; other industrial activities include superphosphate producers of fertilizer, glass manufacturers, and steel manufacturers—all are sources of fluoride emissions.

Several states, including Tennessee, Washington, and Texas, have adopted regulations to protect ambient air and grazing animals. Tennessee does not have vegetation standards.

In addition, the Environmental Protection Agency has developed new source performance regulations for the primary aluminum reduction plants. These were published in the *Federal Register*, January 1976, and are presently the subject of a law suit. The EPA regulations limit fluoride emissions at the point of discharge—the smelter and its control equipment—to 1.9 lbs fluoride per ton of aluminum produced, for prebaked cells.

Controls and monitoring

Chief chemist J. C. Vergho, at the Tennessee plant site, says that real-time, continuous ambient air monitoring is of interest to Alcoa. It provides useful data on the overall operation of a complex production system and its related control equipment.

Vergho points out that Alcoa uses the Alcoa 398 process, a fluidized bed equipped with a baghouse, to control

fluoride emissions. The fluid bed sorbs gaseous fluoride emissions from the smelting cell; then particulate fluoride emissions are trapped in the baghouse.

Engineers, using data from conventional emission monitoring test procedures, evaluated the efficiency of the control equipment. These data on emissions, ambient air, and vegetation provide historical data.

But now, continuous real-time information on emissions can be provided. (Alcoa does not have, as yet, real-time ambient fluoride data.) Real-time implies that data reduction is accomplished by computer on an hourly averaged basis. The advent of automated ambient fluoride instrumentation, using the recently introduced Philips monitor, facilitates monitoring for several reasons:

- Several states (including Washington) require the reporting of ambient fluoride data in the vicinity of the emission point source.
- A reliable, real-time, automated analyzer in the field can save laboratory man-hours.
- Ambient fluoride and meteorological data, coupled with computer modeling and field observations, aid in the assessment of the atmospheric dispersion and downwind impact of fluoride emissions upon receptors.
- As environmental impact assessment needs become more complex, the need for real-time data, rather than a past history of perspective, increases in importance.

A field evaluation of the Philips new HF monitor PW9795 was performed at the Tennessee plant site, since it is Alcoa's policy to evaluate a new monitoring instrument prior to any purchase. In cooperation with Philips personnel, a field trial was conducted with the following criteria for monitoring:

- to locate the monitoring site downwind of the emission point source
- to sample from a common sampling intake, a 30 acfm PVC manifold
- to situate the instruments in a monitoring shelter maintained at 70 ± 5 °F
- to reduce and evaluate the sample data and log maintenance requirements.

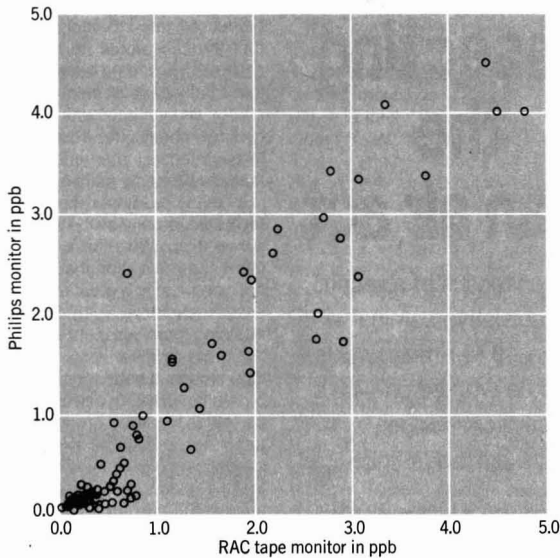
In this program, three test methods

Aluminum Company of America checked its emissions by three techniques and compared the data



Alcoa's Vergho
"adjusting monitor"

Correlation of gaseous fluoride data



Interval ppb fluoride	RAC Dual Tape Monitor No. of Observations	Philips HF Monitor No. of Observations
0.0-0.5	58	70
0.5-1.5	25	11
1.5-2.5	8	12
2.5-3.5	9	7
3.5-4.5	4	4

were compared, two of which yielded data on particulate and gaseous fluoride and one on gaseous fluoride only.

The methods

The fluoride dual-paper tape sampler, the Research Appliance Corp. Model 2356, is designated ASTM Method D 3266-73T, "Automated Separation and Collection of Particulate and Acidic Gaseous Fluoride in the Atmosphere". Two treated tapes, through which the sample stream is drawn at approximately 1 scfm, are indexed simultaneously at a preset interval. The first tape traps particulates. It is impregnated with citric acid and allows the passage of gaseous fluoride, which is then collected on the second tape impregnated with caustic.

The tape-sampler process consists of field collection of the used tapes, subsequent laboratory analysis (particulate fluoride: ash, fuse, distill, and use of an appropriate readout; gaseous fluoride: pretreatment and selective ion readout or equivalent), and data reduction. For hydrogen fluoride the sensitivity and range bracket 2.4 to 90 ppb during 10 to 180 minute sample intervals.

In the Philips HF Monitor, ambient air is continuously scrubbed by an absorption liquid, increasing the gaseous fluoride mass with time. This mass, which is related to the atmospheric HF concentration, averaged over the period since the

start of measurement, is continuously measured potentiometrically, using a fluoride ion-selective electrode.

The measuring periods, and the calibration intervals, may be independently selected from the various ranges. Also, a simple switch setting permits manual, automatic, or remote computer operation. On a 12-h measure cycle, the minimum detectable concentration is 0.12 ppb, with an upper range limit of 60 ppb.

The manual filter and impinger train, ASTM Method D 3267-73T, was used to provide a third comparative method. It consists of a citric-acid-impregnated cellulose filter for particulates, a plated impinger with 150 mL 1.0 N NaOH solution, and mist trap followed by a calibrated dry test meter and a vacuum pump.

Laboratory analysis is similar to the tape sampler: ash, fuse, distill, and use of an appropriate readout for particulate fluoride electrode or equivalent is used to determine the gaseous fluoride in the impinger solution. A typical 12-h impinger train test can determine a minimum concentration of 0.1 ppb, with a relatively unlimited upper saturation range limit for ambient analysis.

Results

During the period October 1–November 30, 1976, 104 direct comparisons were made between data collected by the Philips PW 9795 HF Monitor and the RAC

Fluoride Tape Sampler, Model 2356. Each data point represents a 12-h average in ppb of gaseous fluoride. Both monitors pulled the sample gas from a common positive pressure manifold.

Statistical evaluation of the test results shows the Philips data to have a negative bias in the low range and a positive bias in the high range. In the range of interest, <4.5 ppb gaseous fluoride, the RAC Tape Sampler and Philips Analyzer give comparable data. The actual correlation was Philips Monitor data = RAC Sampler data $- .08 \pm .35$ for 12-h samples.

Table 1 lists test results from four 24-h comparison tests between the two monitors and the impinger train method. Because of its manpower intensity, the impinger train method is seldom used by Alcoa; it is included in this evaluation as a non-instrumented alternative method.

TABLE 1

24-hour comparison test— Fluoride, ppb

Philips	RAC	Impingers
2.50	2.05	3.18
2.56	2.17	1.57
1.96	1.55	1.11
1.76	1.43	1.09

What's ahead

"Because of the benefits of real-time data and an increasing need to use automated test methods to reduce manpower, an instrument such as the Philips HF Monitor has a potentially useful future in the assessment of ambient fluoride around an aluminum smelter", Vergho says.

Over the long term, field reliability of an instrument is perhaps the single most important factor in purchasing an ambient monitor. Both the RAC dual-paper tape sampler and the Philips monitor show excellent field reliability (5% downtime) and low maintenance requirements. Likewise, both instruments demonstrate sensitivity threshold levels below 0.1 ppb on 12-h samples.

OUTLOOK

Dissecting the clean air act

The consensus of a recent APCA legislative seminar was that the 1970 amendments should be worked on with a surgical scalpel, not a butcher's knife

said, their relevance to clean air is being overplayed; that, in fact, the real impact of air pollution control on the economy and energy consumption is minimal. Further, he continued, the costs that are incurred should be paid to protect the public health and welfare.

Ayres noted that a perverse effect of energy conservation and increased coal utilization might well be an increase in air pollution. By example, he cited that possibility that old coal-fired boilers might be kept on-line longer than their life cycle would warrant, with resulting increased air pollution.

Perceptions of the problems

As Charles R. Barden, executive director, Texas Air Control Board, pointed out, the naivety of the times permitted the lawmakers in 1970 to believe that clean air was "just a few short years and easy control measures away." Reflecting this philosophy, the 1970 amendments are long on action and short on perspective. And, Barden said, in many instances, the

"policies have forced us beyond available technology."

Barden felt that public health could not be subordinated to economic feasibility, that the U.S. could no longer afford to squander its energy or air resources, and that a balance must be achieved between energy and environment. But, he felt, this balance should not be achieved solely through federal intervention into matters that are primarily state and local affairs.

With the passing of the 1975 deadlines for achievement of the naaqs, the U.S. sobered up. With the passage of 1975 came the realization that standards were not being met in a great many places, and even more discouraging, the prospects for attaining them were not even in sight.

On the brighter side, the passage of time brought a better understanding of the problems. In 1970, air pollution was perceived as localized problems. With more technical sophistication came the realization that air pollution may not be local, that pollutants may be released in one area and travel long distances to other regions. That, in fact, huge regions may now need to be considered in toto, as one huge air shed, when legislating standards.

Defects of the old act

As Richard D. Grundy, senior professional staff member of the Senate Committee on Energy and Natural Resources stated, "The act addresses abatement of existing sources but it skirts the issues of new growth, significant deterioration (in areas cleaner than required under ambient air quality standards) and nonattainment." The 1970 amendments also never addressed the issue of natural background levels of the six criteria pollutants. This is especially important for oxidants, where natural background levels may at times actually exceed the standard.

Since the old act never addressed the problem of industrial growth in nonattainment areas, Barber said that the EPA has taken to interpreting the act to find workable solutions. EPA's emissions offset (tradeoff) policy, announced only last December, is a prime example. In the absence of new amendments, EPA will probably continue this interpretative approach, Barber said.

Rhoads asked the question, "What do you do about new sources in nonattainment areas?" If you define the phrase "prevention of significant deterioration," Rhoads then queried, "Where do you put new sources after their emissions are controlled as much as possible?" Congress will have to set some criteria soon, he believed. Palomba agreed with Rhoads and added that Congress, not the courts, must provide the policy and the parameters under which and where some deterioration can occur. A clear direction from Congress, he allowed, will permit control programs to be carried forth without the need for litigation.

"Effective and flexible" was the way Walter C. Barber, deputy assistant administrator for air quality planning and standards, EPA, described the 1970 Clean Air Act Amendments to an audience of some 230 air pollution control officials, industrialists and environmentalists attending the Air Pollution Control Association's fifth Government Affairs Seminar in late March. Although this sentiment was echoed by other panelists, flaws in the old act were nevertheless pinpointed for correction in the new set of air amendments likely to be passed this legislative session.

This year's APCA seminar focused on legislative and regulatory problems that have occurred since the passage of the 1970 amendments. In particular the conference addressed two questions: "Is the old act right for today?" and "Is the old act right for tomorrow?" In short, the answer to both was a qualified "no."

Joseph Palomba, Jr., technical secretary of the Colorado Air Pollution Control Commission (and president-elect, APCA) admitted that the old act was a useful and necessary tool but, under it, the country did not achieve all the cleanup that was possible and did not meet the mandated deadlines. As it was necessary in 1970, he said, it is again necessary to set new goals in light of new knowledge.

Richard G. Rhoads from EPA's Office of Air Quality Planning and Standards noted that the old act's framework was good. It set out two key strategies—air quality management and national emissions standards—and three goals—protect the public health and welfare, prevent significant deterioration, and assure that new sources (mobile and stationary) are built properly. Rhoads admitted, however, that the old act needs some updating, some modification.

An intertwining of goals

The goal of clean air cannot be achieved in isolation. The U.S. must also balance its goals for energy independence and economic stability with its striving for clean air. According to Richard Nalesnik, vice president, National Association of Manufacturers (NAM), Congress and the administration tend to ignore these interrelationships.

In Nalesnik's view, the prevailing attitude is that clean air is the imperative to which all other goals must fall in line. But, he felt, this attitude makes tradeoffs very difficult. Barber countered with the statement that "Some path can be found to make the clean air alternative consistent with energy and economic goals." Unfortunately, Barber said, at this point (March 30) we don't know what the economic and energy goals are.

Richard Ayres, staff attorney for the Natural Resources Defense Council, pointed out that these two issues—energy and economics—have played through the clean air act debate in Capitol Hill. But, he



EPA's Barber
"effective and flexible"

At the seminar, the APCA Board of Directors issued a consensus policy statement calling on the EPA to withdraw its emissions offset policy in nonattainment areas until Congress amends the Clean Air Act. And then the EPA should implement only that which is enacted as "a national policy in this area."

Since the old act was vague on matters of control technology and penalties for not meeting standards, new amendments must clearly address the issue of continuous versus supplementary controls, and establish a mechanism for delayed compliance penalties.

If the nation's energy goals are to maximize energy production, then according to Henry E. Beal of the Connecticut Dept. of Environmental Protection, the old act is not compatible with these energy goals. The 1970 amendments place



NAM's Nalesnik
"tradeoffs are difficult"

emission limitations on existing sources and locational limitations on new sources. However, with President Carter's new energy policy, some balancing of energy and environmental considerations will be required in new clean air act amendments to assure that the air amendments are compatible with the energy policy.

Pollution from mobile sources

In the old act, Congress set numbers and deadlines for mobile sources to meet. The automakers claim that they cannot meet the mandated emission schedule and standards.

Automakers claim that the 1978 statutory standards cannot be attained. The industry must begin production of 1978 model year cars this summer. So, according to Congressmen John D. Dingell (D, Mich.), unless Congress acts more rapidly than its usual deliberate pace to set a new mobile emission schedule, the automobile manufacturing cycle will be interrupted, to the economic detriment of the country.

Pending legislation—the Dingell/Broyhill/Riegle/Griffin automobile emissions standards bills, H.R. 4444 and S. 919—is, according to Dingell, less strin-

gent than current standards, more stringent than previously proposed bills, but achievable by automakers.

The new bill would continue the current 1977 model year emission standards—1.5 g/mi hydrocarbons (HC); 15.0 g/mi carbon monoxide (CO); and 2.0 g/mi NO_x—through model year 1979. For model years 1980 and 1981, the standards would be reduced to 0.41 g/mi for HC, 9.0 g/mi for CO but the NO_x standard would be maintained at 2.0 g/mi. For model year 1982, the NO_x emission level would be reduced to 1–2 g/mi, with the final level being set by the EPA; the HC and CO standards would remain unchanged.

If action on the 1977 clean air amendments is not swift, and this appears likely in light of President Carter's recent energy and environment messages, it is almost certain that amendments for mobile sources will be pulled out of the comprehensive clean air bills now being marked up in various congressional committees, and taken through the legislative process separately.

New directions

Congress and federal and state regulators must grapple with the difficult problems of nonattainment, nondegradation and alternative control technology. Yet, underpinning all these issues is the more fundamental issue of the role of the federal government vis-à-vis state and local governments. It seems obvious that the federal government is the least competent to deal with local problems; yet current clean air legislation implicitly or explicitly condones federal preemption of state/local rights, often with the tacit approval of states and local officials.

EPA's Barber felt that the major concern in the next five years should be the definition of roles; the new act should address this issue. Without a clear definition, lawsuits will continue to proliferate.

Rafe Pomerance, legislative coordinator for the National Clean Air Coalition, told the seminar that the key issues being debated on the Hill are:

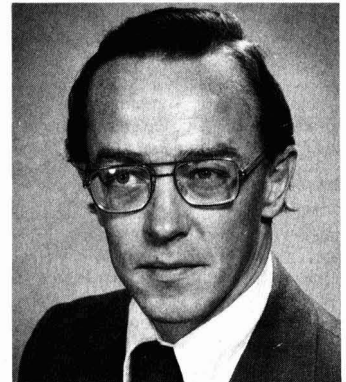
- technology required for new sources; with Congress moving toward the concept of best available control technology
- significant deterioration; with Congress imposing stringent protective measures for national parks and wilderness areas, especially addressing the visibility question, while allowing incremental pollution in other areas of the U.S.
- noncompliance penalties; with Congress attempting to assure competitive equity and bring major sources of pollution into compliance
- new growth in nonattainment areas; the Senate Committee on Environment and Public Works recently approved the

Bentsen (Lloyd Bentsen, D, Tex.) amendment that would permit new sources in dirty air regions under certain conditions.

The Bentsen amendment, strongly opposed by environmentalists, would nullify EPA's offset policy. The intent of this amendment is to permit industrial growth while at the same time attaining a steady downward trend in air pollution. This amendment has already been modified, and it may even be eliminated in a final Senate bill.

NAM's air task force, part of its environmental quality committee, has recommended that the new amendments assure that:

- national ambient air quality standards remain uniform
- expansion of construction, with care, in nonattainment areas be allowed
- supplemental control devices rather than continuous controls be allowed
- timetables be reasonably extended to alleviate severe economic dislocations
- a National Commission on Air Quality be established.



EPA's Rhoads
"a scalpel not a meat-ax"

Set new targets

With industry clamoring for timetable expansions and the Carter administration pushing for increased coal utilization, some thought must be given to a better melding of energy and environmental programs. This is not to deny that the old act has served the nation well. By setting standards and deadlines, the old act provided targets that states and industries could strive to achieve; these targets also provided the public with a benchmark against which to measure progress in air cleanup.

It is just as important for Congress to set targets with the 1977 amendments as it was for them to do so in 1970. But it was clearly felt at the APCA seminar that the old act should serve as a solid foundation for the new act—that, in the words of Rhoads, the old act should be "operated on with a scalpel not a meat-ax." LRE

Validating analytical methods

The AOAC's validation procedures are so rigorous that EPA and FDA confidently use the "official" methods in their enforcement programs, and courts grant the methods preferential status

The Association of Official Analytical Chemists (AOAC) is composed of members who are analytical scientists in government regulatory agencies and associate members who are nongovernment scientists. Yet AOAC maintains no formal membership list nor assesses dues. The AOAC maintains no laboratories, conducts no research, performs no tests. Yet methods officially adopted by the organization receive preferential status in federal, state and other courts, and are used by the EPA and FDA, for example, in their enforcement programs. Why? The answers lie in AOAC's history and rigorous methods adoption procedure.

Broader horizons

With the scientific cultivation of land and the obligatory use of chemical fertilizers, came the need to test the chemical composition of these soil enhancers to assure that they contained the necessary nutrients. From this need for testing, especially with standardized methods of analysis, came the formation of the Association of Official Agricultural Chemists in 1884. Its organizers were mainly scientists with the U.S. Department of Agriculture.

When the technological and legislative complexion of the U.S. changed, the types of methods requiring validation changed too. Methods for the analysis of hazardous substances (including pesticides), foods, drugs and cosmetics were needed, and AOAC's activities were modified to accommodate the new technology and new legislation. Aptly reflecting these changes, the name of the organization was changed in 1965, 81 years after formation, to the Association of Official Analytical Chemists.

Although the bulk of AOAC's testing is now devoted to food, drugs, feeds and fertilizers, there are currently 125 environmentally related topics under investigation. According to AOAC's reckoning, these topics fall into the categories of Pesticide Formulations, Pesticide Residues, and Water. These 125 topics are being investigated by some 117 Associate

Referees who play a pivotal role in the association's collaborative studies.

Because of the rigorous criteria established for the development and testing of analytical methods, AOAC's official methods are well received by scientists, both in and out of government. To illustrate this point: Most of the official AOAC water methods (box) have been adopted as "acceptable for use" for the analysis of chemical pollutants under the National Pollutant Discharge Elimination System administered by the EPA.

A rigorous scrutiny

As the need for new methods or substantial revisions of older methods occurs, AOAC's Executive Office assigns the topic to a General Referee (GR) under whose field of competence the topic falls. The GR, who is a member of the association, in turn appoints a competent scientist to formally undertake the actual investigation. This scientist, known as an Associate Referee (AR), may be a member (governmental analyst) or an associate member (nongovernmental chemist) of the association.



EPA's Meiggs

general referee for water

After careful experimentation, the AR sends the method with precise instructions for conducting the test to competent, experienced analysts in other laboratories. Working independently, these collaborators analyze samples of unknown composition. Their findings either validate the AR's method or cause him to modify the method or devise an entirely new one.

If, after appropriate evaluation, the AR finds the collaborative studies validate his method, he sends a report to the GR with the recommendation that the method be adopted. The GR studies the findings of the collaborative effort and, if in his judgment the method is satisfactory, he sends it on to the appropriate subcommittee of the association with recommendation for approval. The subcommittee, in turn, if it deems it justified, submits the method to the association for approval. This occurs at the annual meeting held every October. If approved by the members at the annual meeting, the method becomes an official AOAC method.

Those methods adopted by the AOAC meet the criteria of reliability, practicality, and availability, and have been validated by collaborative study. Further, the findings of the study are reported in a sci-

Official water methods^a

Acidity^b
Alkalinity^b
Arsenic
Barium
Biochemical oxygen demand^b
Carbonate and bicarbonate
Chemical oxygen demand^b
Chloride^b
Dissolved oxygen^b
Fluoride
Halides
Hardness^b
Iron and aluminum
Mercury^b
Nitrogen^b
Organic carbon
pH
Phosphorus^b
Potassium^b
Silica
Sodium^b
Solids
Specific conductance^b
Specific gravity
Sulfate^b
Trace metals^b
Cd, Cr, Cu, Fe, Pb, Mg, Mn, Ag, Zn

^a Most methods are applicable to drinking, surface, saline water, and domestic and industrial wastewater

^b Method is "acceptable for use" under the NPDES

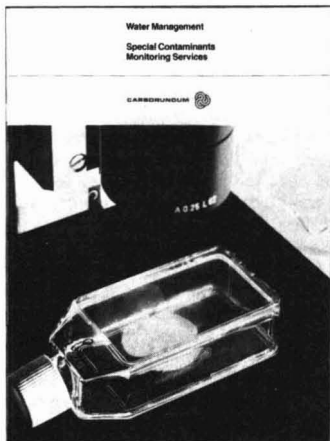
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tific publication, and the method itself is inserted in the association's *Official Method of Analysis*, published every five years; the last edition was published in 1975. However, this latter volume is supplemented annually by *Changes in Methods*, which is a compilation of those methods approved at the annual meeting.

Water methods

Some of AOAC's official water methods date back to 1911, when they were devised to measure parameters of mineral water used for medicinal purposes. In 1970 the emphasis shifted to pollutants in water and the AOAC adopted many of the methods approved by the EPA or its predecessor, the Federal Water Pollution Control Administration.

In 1973, Theodore O. Meiggs, an analytical chemist with the EPA (Denver, Colo.) was appointed General Referee for Water. He now is supervising two Associate Referees who are reviewing all analytical methods (for water) for consideration by AOAC and who are specifically studying: the determination of trace metals by atomic absorption spectrophotometry (Robert Booth, EPA/Cincinnati); and gel permeation chromatography to separate chemical pollutants from fish and other aquatic biota (David L. Stalling, Dept. of the Interior, Columbia, Mo.). These two methods fall under the categories of "Chemical Pollutants in Water and Wastewater," and "Chemical Pollutants in Aquatic Biota," respectively.

The most recent water method was adopted last October for the determination of mercury in drinking, surface and saline waters and in domestic and industrial wastewaters by atomic absorption spectrophotometry. Its detection limit is 0.2-10 µg Hg/L, and has been adopted as "acceptable for use" as an analytical method under the National Pollutant Discharge Elimination System.

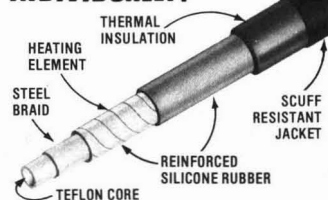
Provides the mechanism

So while the AOAC maintains no laboratories, conducts no research, performs no tests, its members do develop and evaluate methods. But they do this in their official and professional capacities as scientists with federal, state and local regulatory agencies, industrial or consulting laboratories, and colleges and universities. The AOAC simply performs a coordinating function, evaluates the results of the collaborative studies, provides official sanction to acceptable methods and publishes and distributes the methods.

By providing a mechanism to validate rapidly developing technology, by assuring that analytical methods adopted are practical, reliable and reproducible, the AOAC contributes to the public's health and safety and to the protection of the environment in general. LRE

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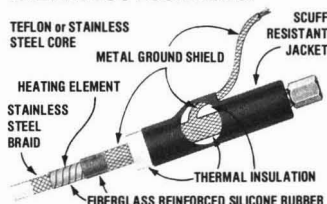
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CIRCLE 17 ON READER SERVICE CARD

Volume 11, Number 6, June 1977 555

Northeastern utilities are meeting the clean air challenge

By installing emission control equipment, building tall stacks, burning lower sulfur fuels, optimizing air/fuel ratios and reducing the operation of some units

Joseph J. Cramer, Frank B. Kaylor, Edward J. Schmidt, and Ernest R. Zabolotny
Stone & Webster Engineering Corp.
Boston, Mass. 02107

The National Environmental Policy Act of 1969 and the Clean Air Act of 1970 have had major impacts on the utility industry, particularly in the highly populated and industrialized northeastern U.S. Yet despite the period of confusion that immediately followed the enactment of these laws, northeastern utilities have been able to achieve considerable control over emissions of combustion products, with significant improvement in the air quality of urban areas.

On a national scale, utilities, regulatory agencies, public interest groups and legislative bodies are now coming to grips with some of the more subtle consequences of the earlier legislation. Questions such as "significant deterioration" and location of new sources in "non-attainment" areas (where national ambient air quality standards have not been achieved) are now being debated. Considering the implications final decisions on these policies will have on national growth and public well-being, the delays are understandable. However, the effect of these delays on utilities has been to create considerable confusion.

The examples described in this article give a broad perspective of the type of environmental problems experienced by northeastern utilities during a period of constantly evolving legislative, judicial and regulatory action. Both urban and non-urban problems, as well as software and hardware analyses, are described. Problems encountered have ranged from nuisance situations associated with existing plants to the more basic consideration of licensing of new units.

Expansion of an existing N.Y. station

The effect of changes in air quality control philosophies between 1968 and 1976 is illustrated by the expansion of the Oswego Steam Station of the Niagara Mohawk Power Co. The station was constructed as a coal-fired power plant between 1939–1951. Four 100-MW units burning eastern coal with sulfur content of 2.5–4% discharged their stack gases through 365-ft stacks after treatment in mechanical dust collectors.

During the late 1960's, the economic and environmental acceptability of coal as a fuel for the station became problematic. Also, the system load of Niagara Mohawk was expanding significantly, and increased generating capacity was needed. A major construction program from 1971–1976 resulted in conversion of the existing coal-fired capacity to oil and the addition of two 875-MW oil-fired units (Units 5 and 6).

Prior to 1970, the State of New York had developed a comprehensive air pollution control program that included a statewide

system of land-use zones, each requiring a specified level of air quality. The zones ranged from heavy industrial areas that allowed the lowest (level V) air quality through pristine areas that required the highest (level I) air quality. The Oswego Station is located in a small upstate city identified as a level III zone. The boundary of the level II zone is, however, less than a mile away, and level I areas are within the influence of the plant.

A second feature of the regulations affected emissions of air contaminants. The primary requirements dealt with the sulfur content of fuels and particulate matter. Particulate emissions for coal-fired boilers were regulated on a sliding scale, with low stack concentrations allowed for larger boilers; for oil-fired boilers, compliance with opacity standards was the governing criterion.

The National Ambient Air Quality Standards, promulgated in early 1971, affected planning for the first 875-MW unit. In 1972 the New York State implementation plan for compliance with federal requirements was filed. Considerable tightening of the New York new source emission regulations affected Unit 6. During 1972–1973, controversy over these standards caused uncertainty over relative emission levels for the various units. The use of oil instead of coal did, however, allow planning and construction to continue since adjustments in fuel specifications could be made with limited effect on plant equipment.

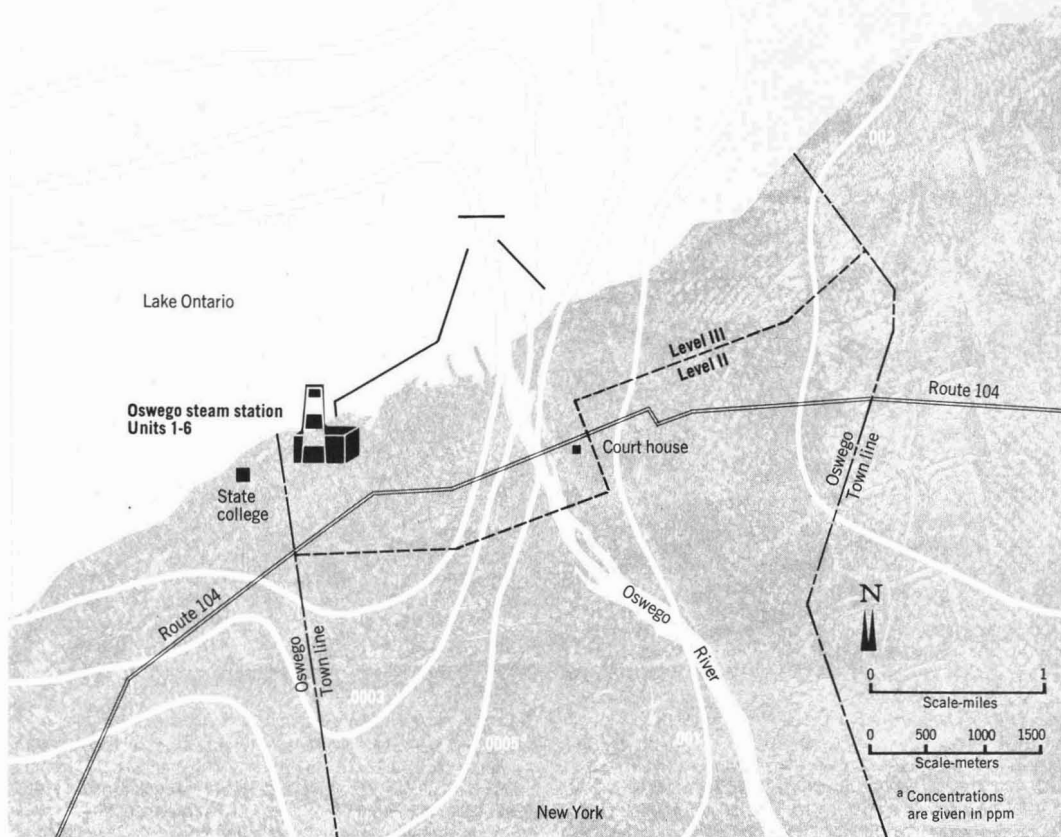
When burning coal, the four original units were unable to meet New York State emission requirements in 1969 without upgrading from the existing mechanical dust collectors to electrostatic precipitators. The mechanical collectors could be retained for oil burning, however.

Because of their size, the potential impact of emissions from Units 5 and 6 would be far greater than that from the four older units. Also, regulations emphasized emission controls for newer and larger units. Alternatives considered included control of both new and old units, of only the new units, and of manifolded common flue gas. The decision was to install high-efficiency electrostatic precipitators on the new units only. The precipitators were sized to maintain low particulate emissions, even with the poorest expected fuel, and to prevent any stack opacity problems.

Other emission controls, in accordance with good engineering practice, were selected to meet air quality standards. Although nitrogen oxide emission standards were not applicable at the time, Unit 5 was specified to emit no more than 250 ppm, which was quite close to the federal new source standard subsequently

FIGURE 1

Predicted annual average SO₂ concentration



required for Unit 6. Sulfur dioxide emissions for all units were to be controlled by the sulfur content of the fuel.

The magnitude of emissions from the expanded plant, together with the proximity of relatively clean "level II" areas, required comprehensive dispersion analyses.

Diffusion climatology in the Oswego area is generally quite good; however, occasionally adverse conditions in combination with the large size of the units and some local terrain features create the potential for higher short-term concentrations. Unstable atmospheric conditions capable of causing rapid downward mixing of the plume can occur fairly often. Also, in spite of a high-stack-discharge velocity, plume rise can be prevented by high-wind velocity under certain conditions.

Full compliance with air quality standards, when burning higher sulfur oil, would require a common 700-ft stack for the four existing units and Unit 5. Alternative strategies included lower sulfur fuel and flue-gas desulfurization. However, the reliability and ease of operation of the tall stack approach were overriding considerations.

Regulatory conditions had changed when the sixth unit was being planned. Emission limits for new sources now required use of 0.75% sulfur fuel, or roughly one-quarter the design value for Unit 5. The governing factors were quite different from those addressed just a few years before. However, analysis of the new unit with the required lower sulfur fuel and the same 700-ft stack height demonstrated that impacts would be acceptable.

The predicted impact of the entire plant is illustrated by the annual SO₂ isopleths shown in Figure 1. Operation of the plant

has confirmed the low contribution of air contaminants to the area, and no air quality standard violations are known to have occurred.

Addition to an existing Boston plant

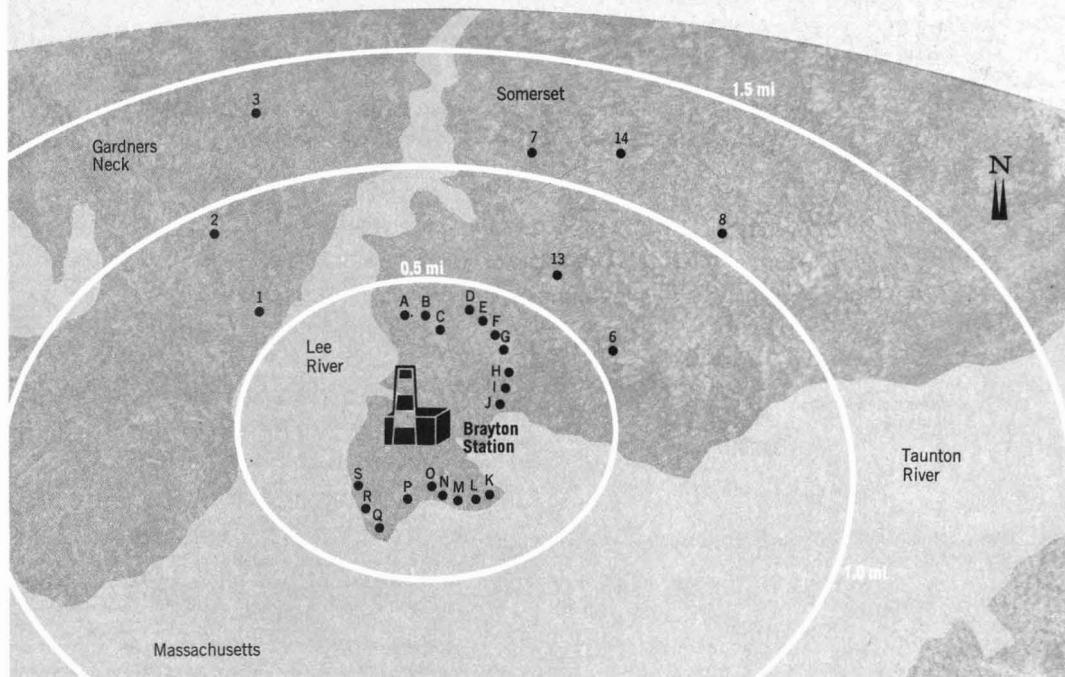
Another example of an existing plant expansion is the Mystic Station of Boston Edison Company (BECO). In 1970, BECO authorized Stone & Webster (S&W) to design and build a seventh fossil-fuel steam-electric generating unit at its Mystic Station. Detailed design and engineering for the new unit were undertaken from 1970-1975. Construction activities began in 1972 and were completed by 1975. Environmental engineering and licensing activities began in 1970, and several post-operational and environmental studies are still under way.

The Mystic Station in Everett, Mass., is about 3 mi north of downtown Boston. The immediate area surrounding the plant is heavily industrialized. Prior to the addition of the new unit (Unit 7), the Mystic Station's existing six units had a total capacity of 618 MW. Initially designed for coal and oil firing during the period from 1943-1961, the units were completely converted to oil firing by 1966.

Applicable emission standards included SO₂ and particulate matter standards of the Boston Metropolitan Air Pollution Control District and new source performance standards for large fuel-burning installations. The ambient air quality standards addressed included state air quality standards and EPA primary and secondary air quality standards for SO₂, suspended particulate matter, and NO_x.

FIGURE 2

Station sites for monitoring sootfall from the Brayton Point Station



Although many federal and state air quality regulations were addressed during design and construction, a non-degradation policy adopted in 1970 by the Commonwealth of Massachusetts posed a major challenge to obtaining a construction permit. Under this policy, the air quality had to be restored and maintained at a "minimal high degree." The interpretation of this policy was that it would be applied to the maximum practicable extent for stack emissions, with strict adherence to the principle of decreased ambient impacts (reduction in ground-level concentrations of SO_2 , NO_2 and suspended particulate matter). This interpretation, which emphasizes ambient impacts rather than emission tradeoffs, is somewhat different from the position currently being espoused by the EPA. The greater flexibility of the interpretation seems to offer considerable advantages.

For the expanded station, two air quality control plans were developed to maintain and/or enhance existing ambient air quality. The primary plan included reduced operation of Units 1, 2, and 3 from 3500 h/y to a projected 500 h/y, installation of flue-gas desulfurization systems on Units 4, 5, 6, and 7, and construction of a 500-ft stack for Unit 7. The alternate air quality control plan also included reduced operation of Units 1, 2, and 3 from 3500 h/y to 500 h/y, reduction in the fuel sulfur content from 0.5 to 0.3% for Units 1, 2, and 3, installation of an electrostatic precipitator on Unit 7 and construction of a 500-ft stack for Unit 7.

Both the primary and alternate air quality plans were approved by the Mass. Department of Public Health, and a construction permit was issued in 1971. Based on the results of a demonstration flue-gas desulfurization system installed on Unit 6, BECO has chosen to implement the alternate air quality control plan for the Mystic Station.

Sootfall from oil-fired plants

In contrast to the more comprehensive cases already described, S&W often handles problems of much more limited

scope. An air quality problem experienced by many northeastern utilities that use fuel oil is particulate matter fallout. Attempts to find satisfactory solutions have been infrequently successful. Through a comprehensive experimental program, New England Power Company, with the assistance of S&W, developed an operational procedure that provides for virtual elimination of sootfall occurrences.

After complaints on fallout were received in the area of New England Power's Brayton Point Station (Somerset, Mass.), extensive field sampling and meteorological data established that the power plant was the source of particulate matter fallout in certain well-defined areas during spring and fall months. Figure 2 shows the location of the plant in relation to the areas monitored. Since sootfall could not be correlated with plant operational procedures, a test program was designed to correlate stack emissions with variations in plant operations.

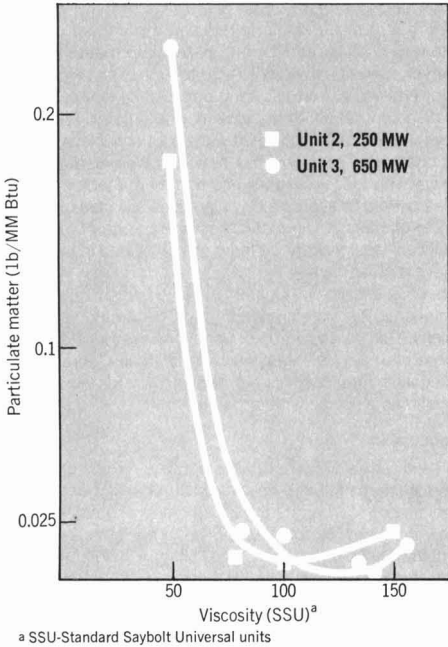
Because of wide variations in fuel oil physical characteristics, precombustion oil temperature was maintained at 250 °F. As a result, the fuel viscosity for proper atomization was not always obtained. Particulate matter effluent as a function of oil viscosity varied considerably from a low in the range of 0.005 lb/MM Btu, with carbon content ranging from 35–85%. The results, shown in Figure 3, indicated that precise control over viscosity is an important factor in optimizing combustion. New England Power now uses viscosity controllers, which are effective under all load conditions.

Transient conditions are frequently cited as possible causes of sootfall. Therefore, these conditions were simulated and tests were performed throughout the entire load range of the units during "light-off," soot blowing operations, and various burner arrangements and firing angles. Only small changes were observed in the rates of particulate matter emissions when compared with rates at corresponding loads under steady-state conditions.

Test results show a rather small but clear trend. As available

FIGURE 3

Particulate load vs. oil viscosity at Brayton Point



oxygen is increased with reduced load, particulate matter emissions are reduced. Carbon monoxide and oxygen monitors were evaluated for their potential as operator tools and were found to be useful in maintaining optimum air/fuel ratios to assure minimum emissions of SO₃, NO_x, and particulate matter.

Four combustion catalyst additives were tested for their effect on particulate matter emissions. Particulate matter concentrations were reduced by 15–30%, with the larger reduction observed for tests run with fuel viscosity at other than optimum

values. Since the effect is most pronounced under conditions that are generally avoided, the usefulness of the additives appears to be greatest during periods of control failures or boiler upsets.

Implementation of the knowledge gained in this test program has provided for essentially trouble-free clear stack operation at the station, and has also been used to alleviate sootfall problems at a number of other utility plants.

Expansion in a sensitive area

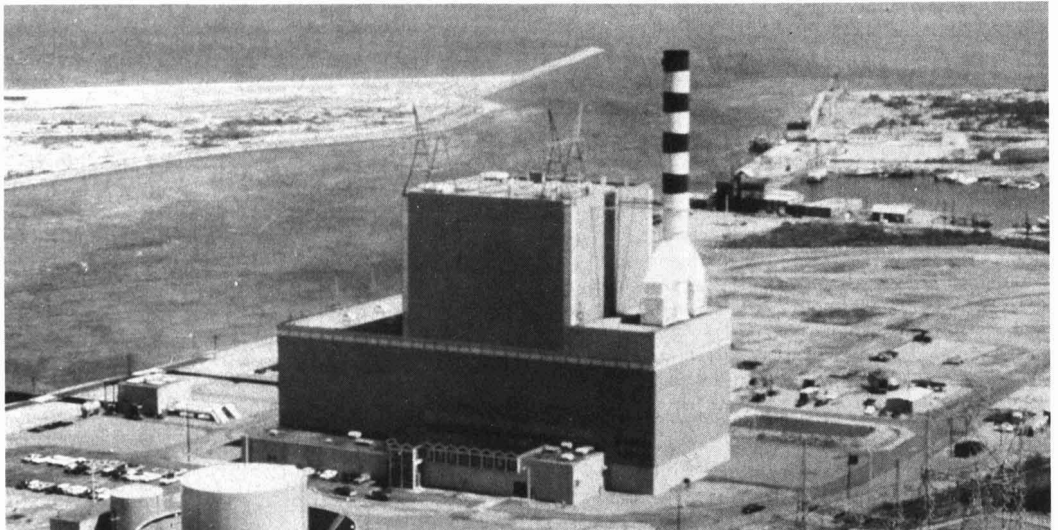
Another example of an existing plant expansion concerned the Canal Plant located in Sandwich, Mass., on the south bank of the Cape Cod Canal, approximately 50 mi southeast of Boston. This expansion required resolving problems similar to those encountered at Oswego and Mystic but, from the standpoint of air quality, involved a more environmentally sensitive area.

In the early seventies, Canal Electric Co. and Montaup Electric Co. initiated plans to jointly construct an additional 560-MW oil-fired steam electric generating unit adjacent to the existing 560-MW oil-fired unit of the Canal Plant. The existing base-loaded unit had been in operation since early 1968. The second unit was to be constructed as a cyclic unit, with commercial operation originally scheduled for late 1975.

Monitoring initiated by the utility in the vicinity of the Canal Plant indicated that annual SO₂ concentrations were far below state and federal standards and 24-h concentrations never exceeded the Mass. standard or the federal secondary standard. However, the state hourly standard (0.28 ppm) in effect at that time had been exceeded on one 3-h occasion at a single monitoring location when the Canal Plant was burning a high-sulfur oil (2.2%). Revisions to the Mass. sulfur emission standards have greatly reduced the allowable sulfur emissions since the period (1970–1971) of the recorded violations.

The addition of a second 560-MW unit burning 1% sulfur fuel oil had the potential of approximately doubling atmospheric emissions from the Canal Station, and adversely affecting ambient air quality. Another design criterion that also required attention was the state non-degradation policy previously referred to with respect to the Mystic Station.

To address these constraints, an extensive stack dispersion analysis was performed. From this study it was concluded that the optimum alternative was to dismantle the existing 300-ft steel stack for Unit 1 and construct a dual-flue 500-ft concrete chimney that would serve both units. Separate flues were selected because of the operating differences of the two units.



Canal Plant. Expansion in a "sensitive" area called for replacement of the original stack and construction of a dual-flue chimney



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The net effect of this stack configuration was to enhance the plume rise and dispersion of the effluents to a degree that would permit both the existing and new unit to burn the maximum allowable 1% sulfur fuel oil and still meet the state non-degradation policy.

The 500-ft stack similarly reduced the impact of other air contaminants such as NO_x and particulate matter emissions. However, it was deemed desirable to further control particulate matter emissions from oil firing because of isolated incidents of acidic soot fallout in the vicinity of the plant. These occurrences were usually associated with upset conditions or extreme load changes. Therefore, the new unit was also designed to operate with low excess air and minimum stack heat losses, made possible by separate insulated flues and stack liners. Also, a highly efficient electrostatic precipitator, one of the first ever specifically designed for oil firing, was included in the design to achieve a clear plume.

These features, in conjunction with sound operating and maintenance practices, are effective in curbing emission excursions. The actual start-up of Unit 2 occurred in late 1975, with commercial operation delayed to early 1976. Compliance with all air quality requirements has been achieved. The plant operates with an extremely clear plume.

In conclusion

The examples discussed some of the problems encountered by northeastern utilities over the last six years. These examples were selected to illustrate the broad range of problems and the manner in which the problems change. In the future, even greater attention may be required in initial siting and selection of generation type. Comprehensive environmental planning will be necessary at a very early stage in the conceptualization of a utility plant project.

Special attention will be required in the northeastern region to demonstrate that new plants or major modifications to existing plants are consistent with environmental goals. Continuous evaluations will become progressively more important to assess the cost and consequences of achieving those goals.



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Alexander Weir, Jr.

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Choose your side.
Scientists of the federal government
and one electric utility
remain at loggerheads
on opacity

Clearing the opacity issue

This is in response to the letter by Don R. Goodwin, EPA's Director of Emission Standards and Engineering (*ES&T*, January 1977, p 10), stating that "Weir et al. . . . misunderstood the purpose and use of opacity standards," and "we consider the article's conclusions to be incorrect." Mr. Goodwin was referring to our paper "Factors Influencing Plume Opacity" (*ES&T*, June 1976, p 539), where we indicated that previously unrecognized variables related to the altitude and azimuth of the sun could result in a power plant meeting New Source Performance Standards for particulate emissions meeting EPA opacity standards in the winter but not the summer, or having a visual opacity of 18% at sunrise, increasing to 85% at noon, as measured in accordance with EPA Method 9.

Mr. Goodwin also stated "However, the results of field studies conducted by EPA (ref. 3) show the positive errors caused by environmental lighting and background contrast are much smaller than suggested by Weir et al. The field studies showed that qualified observers are able to consistently read opacities of black and white plumes with positive errors not exceeding 7.5% opacity based on sets of 25 consecutive readings (ref. 3). The positive errors of this magnitude were infrequent and do not reflect a positive bias in Method 9."

EPA field data

The data from the field studies referenced by Mr. Goodwin do not support these statements. Table 1 indicates that half the certified observers could only read within 7.5% of the meter reading one time out of ten, and two-thirds of the time the observers differed from the meter by more than 10% opacity.

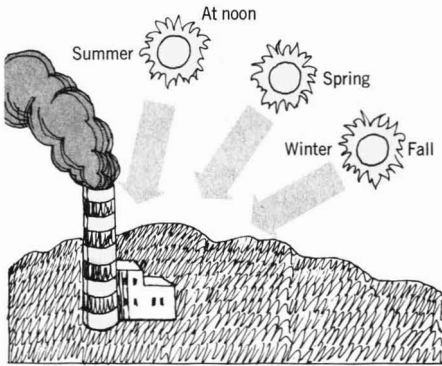
These EPA data do not indicate to the writer that qualified observers are able to *consistently* read opacities of plumes within 7.5% opacity based on sets of 25 consecutive readings, at least on power plant stacks.

The EPA report cited by Mr. Goodwin (ref. 7) ironically offers some confirmation of our thesis that visual opacity is greatly influenced by the position of the sun, both its altitude as well as its azimuth. In the discussion of the "accuracy" of the data from Steam Station Test No. 3, performed September 30, 1974, on Boiler No. 9, and October 1, 1974, on Boiler No. 10 of Duke Power Company's Riverbend Steam Station, the following statement is made on page 28 ". . . the deviations from the meter are calculated for the experimental group as well. The three cases, 45°, 90°, and 0° are treated separately and regression lines calculated for each case. . .

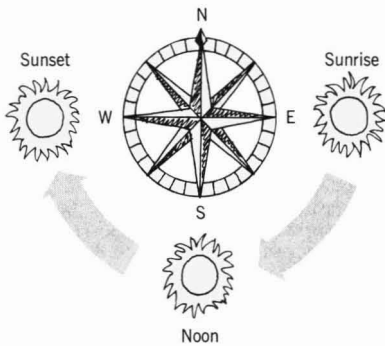
The first line does not have a significant slope while the second two do. However, it is easy to see that the two slopes are different and thus that the observer's determinations differed in the manner and position of observation differed. It is interesting to note that the most accurate readings were made when the group was at an approximate 45° angle to the sun." Our data (ref. 2) on the azimuth effect obtained at about the same latitude (35° N) but at a higher opacity level (the maximum observed opacity in this series of 24 EPA tests was 40.8% opacity) indicate a negligible increase in opacity at noon on the summer solstice (June 21) but a very pronounced influence at noon on the winter solstice (December 21) as shown in Table 2.

It is postulated that if the EPA observations had been made at a higher opacity level or nearer to the winter solstice (December 21) than the autumnal equinox (September 21), a larger effect of azimuth would have been observed. However, since the data were obtained at different times of the day as well as on two different boilers, it is not surprising that the azimuth effect was not quantified in the EPA report. It is perhaps of interest that one EPA observer's set of 25 readings at 9:45 a.m. on October 1 average 18.1% opacity when the transmissometer reading was 36.0% opacity, but this same observer's set of readings average 31.8% at 1 p.m. when the transmissometer reading was 36.9%.

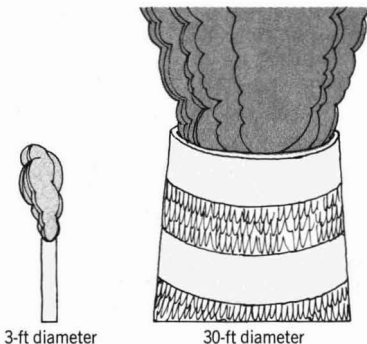
Three basics affecting visual opacity, according to Weir



Altitude. Due to sun light scattering, visual opacity increases as the sun's altitude increases. In summer, the altitude of the sun at noon is 79°; in winter, 33°; spring 56° and fall 34°.



Azimuth. At North latitudes greater than 23.5°, the sun is always due south at noon and is at its maximum altitude. At sunrise and sunset the sun's altitude is zero.



Stack diameter. Visual opacity increases as stack diameter increases even though the grain loading remains constant. Observers trained on small stacks have difficulty with larger ones.

TABLE 1
Data from EPA report on opacity^a

Observer no. ^b	Total observed	NUMBER OF SETS OF 25 READINGS	
		No. with 7.5 % opacity of meter reading ^c	No. which differ from meter by more than 10 % opacity
1	9	4	4
2	9	0	7
3	9	1	6
4	9	3	5
5	9	2	7
6	10	1	7
7	10	2	6
8	10	1	8
9	10	1	7
10	9	2	7
10	94	17	64^d TOTAL

^a 650/4-76-000, page 21, Table 18, "Deviation from Meter Opacity, Steam Station Test 1"

^b Four certified observers were from EPA, four from State of North Carolina enforcement agencies, and two "contractor personnel"

^c Transmissometer readings ranged from 11.6 to 26.1% opacity. Thus a difference of 7.5% opacity represents an "error" of 28.7% at a meter reading of 26.1 or an "error" of 67.5% at a meter reading of 11.6

^d Nineteen of these readings differed from the meter by more than 15% opacity

TABLE 2
Visual Plume Opacity with respect to sun

Angle	VISUAL PLUME OPACITY ^b	
	Dec. 21 at noon	June 21 at noon
0° ^a	54%	85%
(sun behind observer)		
45°	65%	86%
90°	80%	87%

^a Opacity at sunrise or sunset is 18%

^b Particulate emissions in accordance with New Source Performance Standards. Stack diameter is 32.5 ft

These EPA data illustrate the effect of increasing the sun's altitude about 20° on visual opacity. However, since the observer's offset angle was 30° in the morning and 45° at 1 p.m., some of the increase in observed opacity must be attributed to the azimuth effect. Perhaps the most significant conclusion in the EPA report is that "the observer's determinations differed when the manner and position of observation differed."

The conflict

Thus the EPA field studies cited by Mr. Goodwin do not support his statement, "The effects of geographic location, time of day and other illumination variables do not significantly affect the ability of trained observers to accurately evaluate plume opacities." Mr. Goodwin's statement that "the field studies were done by certified observers who were trained at different geographic locations . . ." illustrates a complete lack of understanding of the influence of light scattering angle and thus the altitude of the sun on what a visual observer would see.

It is not the geographical location where the observer was trained but the geographic location of the stack that is important. Like our studies on the effect of sun azimuth, the effect of latitude is more pronounced in the winter than in the summer. A decrease in North latitude of the stack from 56°N to 24°N results in an increase in plume opacity from 30% opacity to 65% opacity at noon on December 21, but the same plume at noon on June 21 would only increase from 75% opacity to 88% opacity for the same latitude decrease. Thus a power plant emitting the

same amount of particulate matter of the same particle size would have a more difficult time meeting opacity standards in Florida than in Alaska.

However, this is not just an academic argument concerning the influence of the sun's altitude on plume opacity. The EPA viewpoint can result in the expenditure of hundreds of millions of dollars by industry to meet opacity standards that are more restrictive than mass emission standards and result in raising the price of concrete, steel, and electricity to consumers. Mr. Goodwin stated, "Another point of concern to EPA is that Weir et al. apparently misunderstood the purpose and use of opacity standards . . . opacity standards are set at levels that are not more restrictive than the corresponding mass-emission standard."

Weir's position

Our data indicate that a new coal-fired power plant could meet EPA's New Source Performance Standards for emission of particulate matter with a grain loading of about 0.046 grains per standard cubic foot. However, this concentration would have a plume opacity of about 85% in a 32.5-ft diameter stack at noon on June 21, assuming a mean particle diameter of 2.6 microns.

In order to meet EPA's 20% opacity standard the year round, the grain loading would have to be reduced from 0.046 to about 0.007 grains per standard cubic foot if the mean particle size was unchanged. However, since additional control equipment would result in removing more of the larger particles, the mean particle size would change, and thus a grain loading of about 0.003-0.005 grains per standard cubic foot would be required to meet 20% opacity, which is about one-tenth the mass emission required by EPA's New Source Performance Standards.

In conclusion, we have examined the report of the field studies referenced by Mr. Goodwin and do not find any EPA data that invalidate the conclusions of our article, and, as a matter of fact, some of the EPA data taken at a power plant support our thesis on the influence of the sun's position on visual plume opacity. On a constructive note, the change in the EPA position (ref. 3) on the use of transmissometers to measure opacity is a welcome one as is the statement that Ringelman number is no longer considered by EPA to be equivalent to opacity.

Additional reading

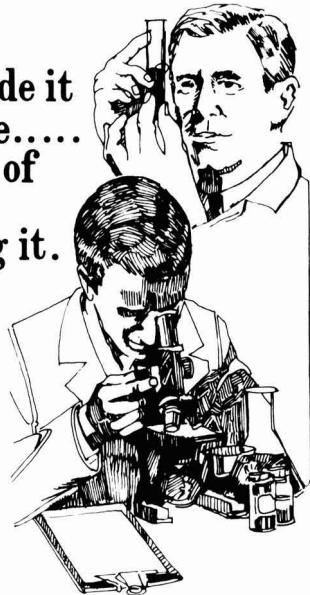
1. Hamil, H. E., Thomas, R. E., and Swynnerton, N. F., "Evaluation and Collaborative Study of Method for Visual Determination of Opacity of Emissions from Stationary Sources" Environmental Protection Agency, Research Triangle Park, North Carolina, EPA Report No. 650/4-75-009, January 1975, 70 pp.
2. Weir, A., Jr., Jones, D. G., Papay, L. T., Calvert, S., and Yung, S., "Measurement of Particle Size and Other Factors Influencing Plume Opacity" presented at International Conference on Environmental Sensing and Assessment, September 14-19, 1975, Las Vegas, Nevada. Sponsored by U.S. World Health Organization, U.S. EPA, American Chemical Society, and others.
3. Goodwin, D. R., "Public Comment Summary: Opacity Provisions under Standards of Performance for New Stationary Sources of Air Pollution" U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. 27711, August 1975, p. 24.



Alexander Weir, Jr. is the inventor of the WEIR Scrubber (*ES&T*, June, 1976, p. 534), which was the first SO₂ scrubber in the U.S. to meet the National Academy of Engineering's criteria of "successful operation for over a year at a size larger than 100 megawatts." He has been a member of the American Chemical Society for 33 years and received his Ph.D. in chemical engineering from the University of Michigan. He is the Manager, Chemical Systems Research and Development, for SCE.

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Air monitoring with tunable lasers

Because of their unique capabilities, tunable lasers offer an added dimension to air pollution surveillance, especially in remote sensing and in situ monitoring

E. David Hinkley
Laser Analytics, Inc.
Lexington, Mass. 02173

Conventional instruments are not always suitable for monitoring atmospheric pollutants, and advanced instrumentation based on physical processes, such as those involving tunable lasers, is needed. Several monitoring schemes are possible with tunable lasers: resonance fluorescence, resonance scattering, resonance Raman, differential absorption, and laser heterodyne (see Additional reading, Hinkley, Ed.).

Resonance fluorescence and scattering have been most useful for detecting atoms and molecules at high altitudes or in reduced-pressure chambers where the fluorescence is not severely quenched. Resonance Raman has so far been applied to only one or two gases, although the related CARS (coherent anti-Stokes Raman scattering) technique is gaining acceptance as a way to remotely measure engine and stack effluents. This article, however, will concentrate mainly on the differential absorption technique because of its high sensitivity and broad potential applicability for pollutant monitoring.

Resonance absorption occurs when the wavelength (frequency) of electromagnetic radiation coincides with the center frequency of an absorption line of an atomic or molecular species. For monitoring applications, the differential absorption between radiation alternately tuned on and off the absorption line provides a direct measurement of the pollutant concentration over the path.

One of the often overlooked advantages of the differential absorption technique is the inherent relative ease of calibration, which arises from the fact that the *optical thickness* (logarithm of absorbance) of a path is equal to the product of pollutant concentration, absorption cross-section, and pathlength. For example, if a measurement is made over a 100-m path of a pollutant gas whose ambient concentration is 1 ppb (10^{-9} v/v),

the optical thickness is identical to that which would obtain for a 1 ppm (10^{-6} v/v) specimen of the gas (at the same total pressure) in a 10-cm cell. It is generally easier to prepare a stable sample of 1-ppm concentration for calibration than a 1-ppb concentration sample that may be required for a non-optical monitoring technique.

There are essentially four different monitoring schemes that use the differential absorption technique (Figure 1):

- active bistatic system involving a cooperative reflector or remote detector
- active monostatic system involving a natural or topographic reflector
- active monostatic system involving aerosol backscattering (this may also be bistatic if the detector is situated away from the laser transmitter)
- passive monostatic system involving heterodyne detection.

The term "bistatic" refers to an arrangement in which some of the equipment is positioned at a distance from the laser, while in a "monostatic" system, all equipment is at a single location. (For an article covering other types of laser sensing, see *ES&T*, January 1977, Melfi et al.)

Tunable lasers for monitoring

Both fixed-frequency and broadly tunable lasers are useful for atmospheric monitoring. The distinction between the two types is not so clear as one might at first believe. A reasonable definition of a *broadly* tunable laser is one that is continuously tunable over 1 cm^{-1} or more and has a total tuning range of hundreds of cm^{-1} . A fixed-frequency laser is one that cannot be tuned over more than a small fraction of a cm^{-1} (about 0.002 cm^{-1} for a low-pressure CO_2 laser, for example). A fixed-fre-

FIGURE 1

Laser monitoring techniques based upon absorption spectroscopy

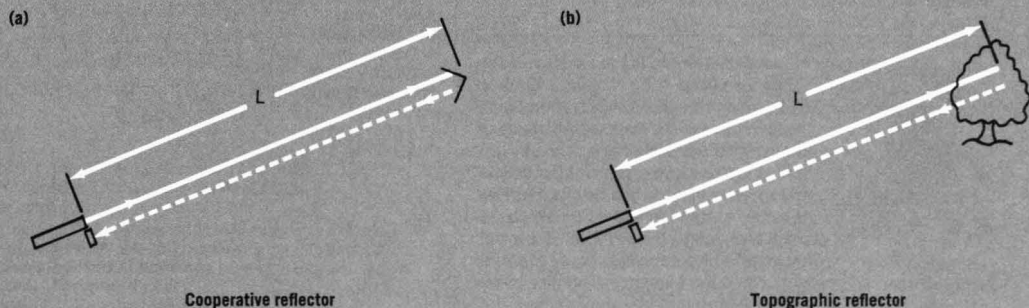


TABLE 1.

Tunable lasers, their properties and potential monitoring applications

Tunable source	Wavelength region (μm)	Typical power (W)		Probable monitoring applications
		cw	pulsed	
Dye laser	0.34–1.2	10^{-1}	10^8	Resonance fluorescence (atoms, molecules) Differential absorption/Mie backscattering
OPO	0.55–3.5	10^{-2}	10^5	Differential absorption/topographic backscatter
Diode laser	3–30	10^{-3}	1	Differential absorption/cooperative reflector Remote heterodyne detection
SFR laser	3(HF-pumped) 5–6 (CO-pumped) 9–14 (CO ₂ -pumped)	1	10^3	Differential absorption
HPG laser	9–11 (CO ₂)	—	10^5	Differential absorption/natural reflectors

quency laser may often be step-tuned from one transition to another, but the resulting total *continuous* coverage is typically only 0.1 cm^{-1} over a 100 cm^{-1} interval.

At sea level, individual absorption lines of atmospheric gases are $0.2\text{--}0.3\text{ cm}^{-1}$ wide; but for gases such as SO_2 , where adjacent pressure-broadened lines overlap, tuning over $0.5\text{--}1\text{ cm}^{-1}$ may be needed to reveal characteristic spectral features. At higher altitudes, line-widths are smaller, approaching the Doppler limit at the stratopause.

Broadly tunable lasers usually possess some method for controlling gross tuning as well as fine tuning of the laser frequency, either by choosing the frequency (wavelength) range (changing composition in the case of semiconductor lasers, changing dyes in dye lasers) or by changing the operating conditions (tuning to the center of the transition by temperature or magnetic or electric field, or controlling the wavelength dependence of the cavity with prisms or gratings). Fine control of the laser wavelength involves tuning a single cavity mode with an etalon, or by small changes in temperature, magnetic field, or electric field.

The power capability, mode quality, and pulse characteristics are also important considerations in selecting a laser for a particular monitoring application. Table 1 illustrates some of the main features of tunable lasers that have been used for air pollution monitoring.

Dye lasers operate in the visible and near-ultraviolet and infrared by optical pumping (via flashlamp or laser) from the ground state to an excited singlet electronic state of high rotational and vibrational energy. Because of the high-density levels of the large dye molecules and the large widths of these levels in solution, very broad and continuous bands of radiation are emitted, typi-

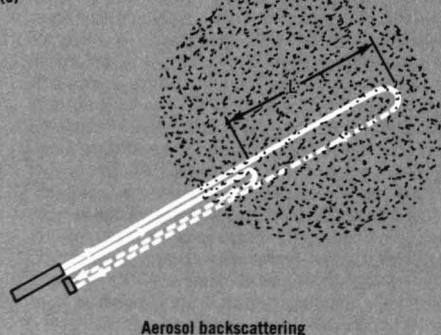
cally 50 nm wide. In order to narrow the laser line-width, yet permit tunability within the broad emission band, highly frequency-selective optical resonators are used.

Dye lasers now available commercially from several manufacturers can be used in the visible and ultraviolet for atmospheric monitoring of a limited number of pollutants— SO_2 , NO_2 , O_3 —by differential absorption or fluorescence. Because of the high-power capability of dye lasers (Table 1), it has been possible to detect Na and Ca above the stratosphere by resonance scattering with a ground-based system.

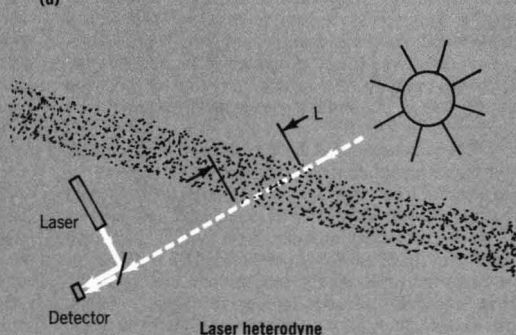
The *optical parametric oscillator* (OPO) consists of a pump laser that emits radiation in the visible or infrared, and a nonlinear birefringent crystal. The output frequency is a function of the unique conditions required to simultaneously satisfy energy and momentum conservation for the parametric process within the pumped crystal. Tuning is achieved by rotating the nonlinear crystal, varying its refractive index through temperature changes, or applying pressure or an electric field. A commercially available lithium niobate oscillator operating in the $0.55\text{--}3.5\text{ }\mu\text{m}$ region achieves about 0.01 cm^{-1} resolution by using a thermally tuned interferometer. The development of cadmium selenide and proustite parametric oscillators is expected to provide high-pulsed-power lasers for the 3.5 to $20\text{-}\mu\text{m}$ region.

Semiconductor *diode lasers* are the simplest of the tunable lasers; they provide modest power with narrow line-width, good amplitude and frequency stability, and are tunable over a relatively wide spectral range. They require cryogenic cooling, however, and do not yet have the controllable qualities of the other, more complex tunable lasers. Diode lasers have been used extensively for high-resolution spectroscopy for several years, and commercial units are now able to cover the important

(c)



(d)



infrared "finger-print" region between 3–20 μm .

Tunable diode lasers have been produced with single-mode output as high as 50 mW in the 5- μm region and 5 mW in the 10- μm region, and continuous wave (cw) operation is now possible above liquid nitrogen temperature (77 °K). These lasers have been used extensively in: reduced pressure-point monitoring, in situ source monitoring, and long-path ambient air monitoring.

Additional tunable lasers

Spin-flip-Raman (SFR) lasers can provide high power cw or pulsed-tunable radiation having excellent spatial-mode quality. Spectral coverage is somewhat limited, and good frequency stability is difficult to achieve. In addition, the apparatus is rather complex and cryogenic temperatures are required.

In a SFR laser, light from a fixed-frequency laser is inelastically (Raman) scattered by electrons in a semiconductor crystal. An applied magnetic field causes an energy-level separation between electrons whose spins are aligned along the field and those of oppositely directed spins. When the incident radiation excites an electron into a higher energy state, the scattered radiation has a lower frequency and is called the Stokes component. Conversely, when the incident radiation induces an electron to shift to a lower energy state, the scattered radiation is at a higher frequency and is called the anti-Stokes component. These components, as well as some weaker ones, can be used in spectroscopic and monitoring applications. An InSb SFR laser at 5 μm has been used in conjunction with an opto-acoustic detector to observe NO in automobile exhaust and in the atmosphere. In addition, stratospheric NO and H₂O were detected with a similar balloon-borne system.

Molecular *gas lasers*, such as CO₂, have most frequently been operated at pressures of around 10 Torr where the gain bandwidths are essentially Doppler-limited to approximately 0.002 cm⁻¹. In order to increase the range of continuous tuning, higher pressures are needed to broaden the gain bandwidth.

Several approaches for achieving high-pressure operation of gas lasers are currently being studied. One of these is the transversely excited atmospheric (TEA) configuration laser with ultraviolet pre-ionization, and another is the capillary laser. Small-bore capillary lasers have operated at pressures of several atmospheres, yielding continuous tunability over almost 1 GHz (0.033 cm⁻¹).

High-pressure gas lasers have relatively high peak and average powers, and should be particularly useful in differential absorption systems involving non-cooperative target backscatter. Because of the excellent quality of the beam from a capillary laser, it is also useful as a local oscillator for heterodyne detection, and was recently used successfully in this manner in an airborne-ground reflection experiment.

Laser systems, proposed applications

An *active bistatic system* is typically one in which the laser transmitter and receiving telescope are combined, and an efficient retroreflector is placed remotely (Figure 1a). This technique, often called the "long-path technique for ambient air monitoring," is based on the absorption of laser radiation by a molecular species along the path of the beam; it provides a measurement of the average or integrated-path concentration of a pollutant gas between the laser and retroreflector. It has the important advantage of permitting low-power lasers to be used.

The long-path data have aided the evaluation of mathematical models for the concentration, diffusion, and transport of atmospheric pollutants. Grid sizes of these models are typically around 1 km, which corresponds well to the laser path-lengths normally required. Range information (pollutant concentration vs. distance) can be obtained by positioning several retroreflectors at different locations. Where comparative measurements have been made with standard monitoring instruments, the agreement has generally been good when meteorological conditions tended to produce a uniform pollutant concentration.

FIGURE 2

Laser monitoring vs. point monitoring of atmospheric CO

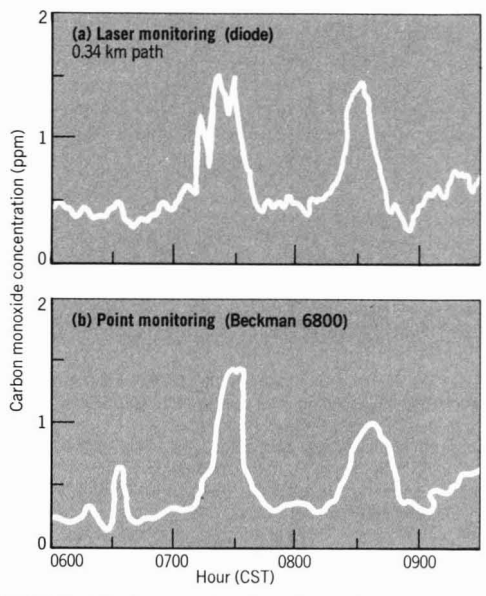


Figure 2, for example, shows a comparison between continuously-recorded long-path (0.34 km) data of atmospheric carbon monoxide measured by a tunable semiconductor diode laser to the 60-s averages of a point-monitoring instrument stationed at one end of the path. (These data were obtained in St. Louis, Mo., as part of EPA's RAPS program). The source of the two plumes of atmospheric CO recorded at 0730 and 0830 is not known, but the agreement between the long-path laser data and the point monitor is evident, both in time and concentration.

Long-path monitoring of several gaseous pollutants has been performed by using path-lengths to over 3 km and a variety of cooperative reflectors; and the availability of sensitive detectors means that low-laser power levels (typically 1 mW for distances of several km) are adequate. This is important not only in permitting a variety of lasers to be used (diode lasers), but also from an eye safety standpoint as well. The ability to measure changes in transmission of 0.3% or less has been reported. This means that for gases that have large cross-sections, a detection sensitivity of a few ppb is possible over a 1-km path. Advances in signal processing are expected to improve sensitivity even further.

The *active monostatic system* (natural reflectors) (Figure 1b) uses existing targets of opportunity such as foliage, terrain or buildings to reflect laser radiation back to the receiver. It has the advantage of permitting long-path measurements to be conveniently made along different directions and with varying path-lengths; it is limited only by the availability of suitable targets. However, because of the inefficient collection of radiation scattered from these distant natural targets, the system requires relatively high-laser power.

Demonstration experiments involving natural-target backscatter have been performed with fixed-frequency and tunable lasers that use both direct and heterodyne detection. In the first such measurement actually showing the absorption line profile of a pollutant gas, Henningsen et al. detected CO by using a 20- μJ tunable OPO, detecting backscattered radiation from foliage more than 100 m away.

The *active monostatic system* (aerosol backscattering) in

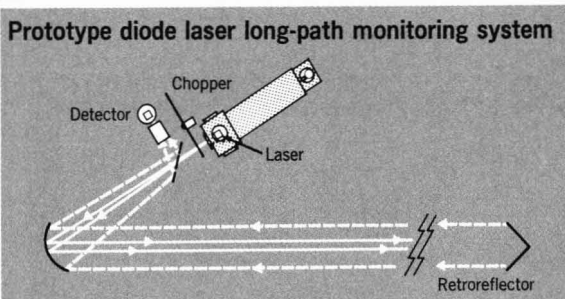
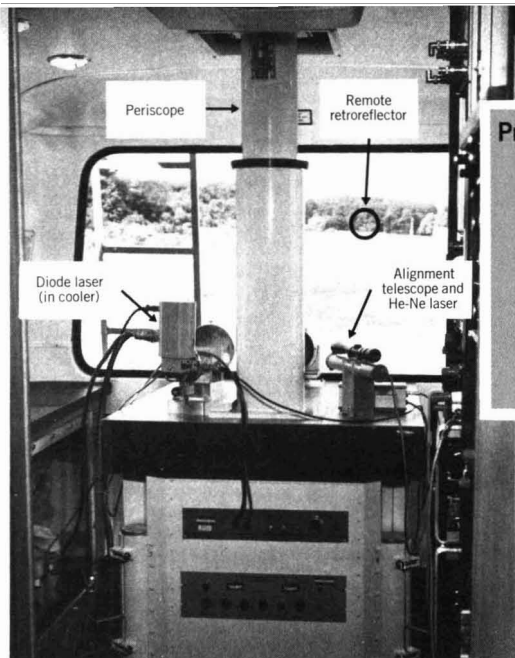


Figure 1c involves the detection of laser radiation scattered by atmospheric aerosol particles, and is commonly known as Differential Absorption Lidar (DIAL). The received laser power scattered by these particles permits a measurement to be made of pollutant concentration by tuning the laser alternately between regions of high and low absorption. Range information is obtained by interpreting the return signal as a function of time.

The laser power requirements for a DIAL system are substantially higher than for either of the techniques already described. Although there is a great deal of ongoing development work in the field of high-power tunable lasers (Table 1), only the dye laser has been able to provide sufficient power for DIAL monitoring. Other DIAL measurements have used discretely tunable lasers.

Heterodyne detection is the most sensitive means of detecting infrared-laser radiation, and it can be useful for broadband radiation as well. By using a tunable laser as local oscillator, absorption lines of pollutant gases between the source and a heterodyne receiver can be fully resolved in the manner shown in Figure 1d. The laser power requirements for achieving the ultimate heterodyne detection sensitivity (which is many orders of magnitude better than for direct detection), is typically around 1 mW, and any of the lasers listed in Table 1 can be used.

Because of its sensitivity, heterodyne detection is being considered for measuring the weak laser return signal radiation that exists in monitoring schemes such as those based on topographic and atmospheric aerosol backscatter. Moreover, in certain cases where the laser power needed for a direct-detection system would necessarily exceed the allowable standards for eye safety, heterodyne detection will permit considerably less laser power to be used. In the scheme illustrated schematically in Figure 1d, the sun serves as the source of radiation and the heterodyne receiver tunes through characteristic absorption lines of pollutant gases in the intervening atmosphere, mainly the Earth's troposphere and stratosphere. It should be noted that over the past several years, spectrometers and interferometers have been used to remotely measure *emission* and *absorption* lines of such gases, but the laser heterodyne technique now permits such measurements to be made with unsurpassed resolution and sensitivity.

The altitude dependence of the gas concentration may be obtained by measuring the width(s) of the pressure-broadened spectral lines(s) being monitored. By using this technique, in early 1976 Menzies and Seals measured the height distribution of ozone with a discretely tunable CO₂ laser mounted on a heliostat.

Later in 1976, Frerking and Muehlner performed a similar measurement with a continuously tunable semiconductor diode laser. This laser heterodyne detection technique complements the interferometric and dispersive radiometric measurements that have already proved valuable for remote sensing, and may lead to an important set of instruments for ground-based monitoring of the lower and upper atmospheres.

Commercial availability

As yet, there are no commercial tunable laser systems designed specifically for any of the pollution monitoring applications described here. Several prototypes have been constructed, however, such as the tunable diode laser long-path system shown in Figure 3.

The tunable lasers themselves are now available commercially. Their prices vary widely, depending on specific performance requirements involving tradeoff between tunability, line-width, power, and duty cycle. For dye lasers, prices generally range from \$10 000–\$45 000. Optical parametric oscillators, \$25 000–\$55 000; and diode laser systems, \$16 000–\$50 000. Spin-flip Raman lasers start at \$20 000, and prices of high-pressure gas and capillary lasers start at around \$10 000.

Summing up

Air pollution monitoring with tunable lasers is gaining widespread acceptance. The lasers offer unique capabilities related to remote sensing and in situ monitoring; the systems are generally simple and straightforward to calibrate.

Historically, progress in this field has been largely instrument-limited: lasers with limited power, tunability, stability; signal detection techniques with inadequate sensitivity or speed; computers with limited capabilities or field reliability. Improvements continue to be made in all of these areas in laboratories of many countries. It appears certain, therefore, that laser monitoring of pollutants in the troposphere and stratosphere will become increasingly important for our understanding and surveillance of the atmosphere.

Additional reading

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Coordinated by LRE

Optical systems unravel smog chemistry

New insights into old problems on chemical transformations in photochemical smog are provided by tunable lasers and long path FT-IR spectrometers

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Application of tunable lasers and infrared Fourier transform spectroscopy to atmospherically important systems has led to the identification and quantification of a number of species in smog chambers, in laboratory experiments, and in the polluted troposphere. Many of these are labile molecules or free radicals whose presence had been previously postulated on sound kinetics and mechanistic grounds, but not directly observed. Others had not even been suspected to exist in atmospheric systems. Additionally, the development of tunable lasers has greatly aided elucidation of the mechanisms of certain important atmospheric reactions, including primary photodecomposition processes.

The identification and accurate measurement of the primary pollutants, intermediates, and products in photochemical air pollution continues to be a high priority in atmospheric and related laboratory studies. Such an improved data base is not only essential for a better understanding of the complex chemical and physical transformations involved, but is also necessary if future oxidant control strategies are to be made more cost-effective and responsive to the complex trade-offs between energy, environmental, and economic constraints (*ES&T*, May 1977, p 456).

Those familiar with the approach traditionally taken by chemists in unraveling the details of reaction mechanisms in the laboratory will readily understand the need to obtain improved analytical information. Without detailed knowledge of the nature and concentrations of the intermediates and products, the mechanism of even a relatively simple laboratory reaction cannot be considered valid. The extent of the challenge facing atmospheric chemists becomes clear when one recognizes that similar information must be obtained for an incredibly complex heterogeneous reaction system involving hundreds of different species. Some of these are stable while others are highly reactive, with lifetimes of the order of seconds or less. All interact in a diurnal cycle that includes periods of both light and dark—and at concentrations in the part per million (ppm) range at most, and more frequently in the part per billion (ppb) range for molecules, and even lower for free radicals.

Thus the validation of complex computer kinetic models of photochemical smog, which are becoming increasingly important in the development and implementation of oxidant control strategies, and which often involve a hundred or more reactions, demands identification and measurement of a large number of species.

While traditional wet chemical methods have yielded valuable information in the past about the nature and concentrations of the major species involved in photochemical smog—to an increasing extent during the past 10 years—sensitive and specific physical techniques have been developed and applied. Thus, it is only recently that some of the important short-lived intermediates and labile products, postulated in the past, have been identified and quantitatively measured. The advances in this area are due in large measure to the development of high resolution optical detection techniques such as tunable lasers and Fourier transform infrared spectroscopy (FT-IR).

For example, the development of ultraviolet tunable dye lasers was necessary for the direct detection of at least one key intermediate species, the hydroxyl radical, in photochemical smog. Such lasers are also used in the elucidation of the wavelength dependence of the photodecomposition modes of important pollutant molecules. The latter absorb solar ultraviolet radiation in the troposphere ($\sim 290 < \lambda < 400$ nm) and dissociate to produce radicals or atoms capable of initiating the photooxidation of organics.

The use of lasers for the remote monitoring of certain primary pollutants such as CO, NO, NO₂, and SO₂ has been discussed in the companion article by Hinkley (this issue), and by others. Thus we shall emphasize, instead, recent studies with tunable lasers and Fourier transform infrared spectroscopy, in which certain free radical and labile molecular species present in ambient and simulated atmospheres were directly identified and measured. These species are significant in oxidant control either because of their mechanistic role in establishing kinetic computer models, or alternatively, because of their potential effects on health and visibility, or both.

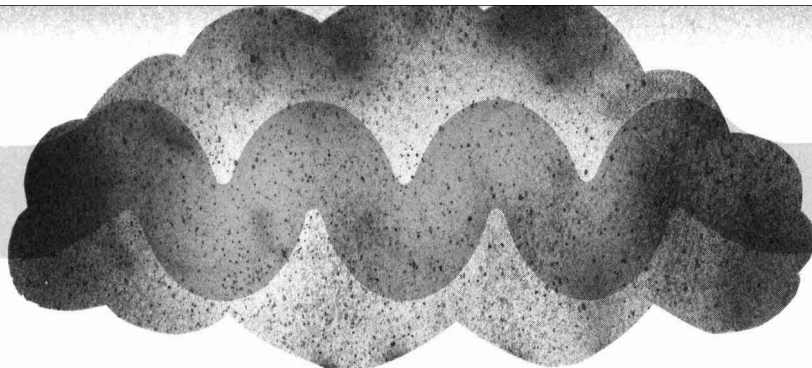
Discussion of combined gas chromatography–mass spectrometry, a powerful analytical tool that has been successfully applied to the determination of many relatively stable atmospheric species (including particulates), is beyond the scope of this feature.

UV tunable dye lasers

Several unique properties of lasers make them especially useful in analytical, kinetic, and mechanistic studies of polluted atmospheres. These properties include:

- the capability of “tuning” the radiation of certain lasers over selected wavelength regions in the infrared, visible, and ultraviolet regions
- the generation of highly monochromatic radiation with little spatial diffusion of the beam (extremely good collimation)
- the availability of a wide range of power outputs (photon flux) ranging from relatively weak to extremely intense radiation.

A notable achievement made possible by the development of lasers has been the recent detection and measurement in ambient air of low steady-state concentrations of the hydroxyl



An FT-IR spectrometer consists of an infrared source, a detector sensitive in the infrared region, and three interferometers sharing a common mirror drive.

In its simplest form, an interferometer consists of a fixed mirror, a moving mirror, and a beam splitter. A portion of the light rays striking the beam splitter are sent to the fixed mirror and the remainder to the moving mirror. The rays of light are reflected by the respective mirrors back to the beam splitter where they recombine. As the beams recombine, light of each wavelength undergoes a series of constructive and destructive interferences that depend upon the difference in distance traveled to the fixed and moving mirror. As a result the detector sees an "interferogram"—the superposition of audio sinusoids from all the individual wavelengths.

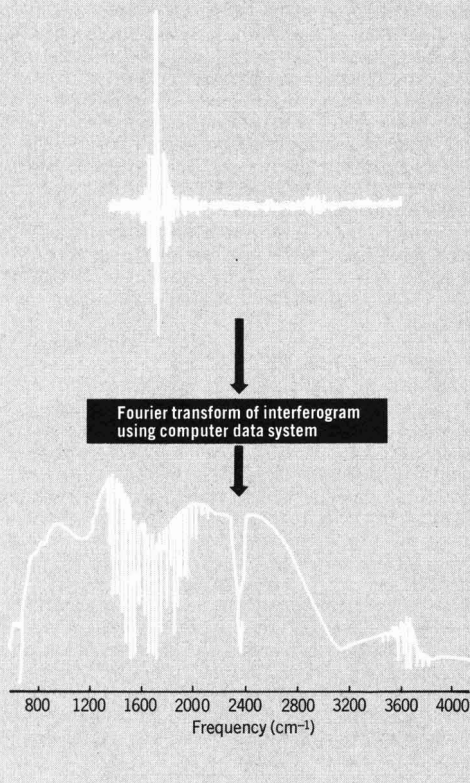
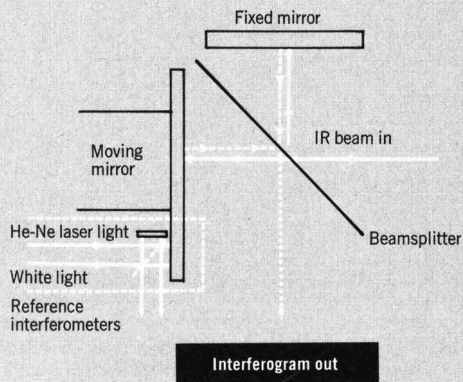
A plot of intensity vs. optical wavelength, the familiar IR spectrum, is extracted from the interferogram through a mathematical formalism known as the Fourier transform, a calculation so complex that it is only practical with the use of a computer.

How it works

The main interferometer operates on a large diameter infrared beam. Two smaller "reference" interferometers are used to control the sampling of data in the infrared interferogram. One reference interferometer employs a small He-Ne laser which, because its radiation is monochromatic, provides an interferogram that is a simple sine wave. The position of the moving mirror is accurately monitored by counting the number of whole wavelengths in this sine wave, and sampling of the infrared interferogram is thus performed at equal intervals of distance as the mirror travels through a scan.

The second reference interferometer uses a beam of white light. The most intense portion (or "center burst") of the white-light interferogram is used to start data collection for the infrared interferogram at the same position of the moving mirror for each scan. Thus, accurate averaging of many scans can be achieved over long periods of time.

What's FT-IR ?

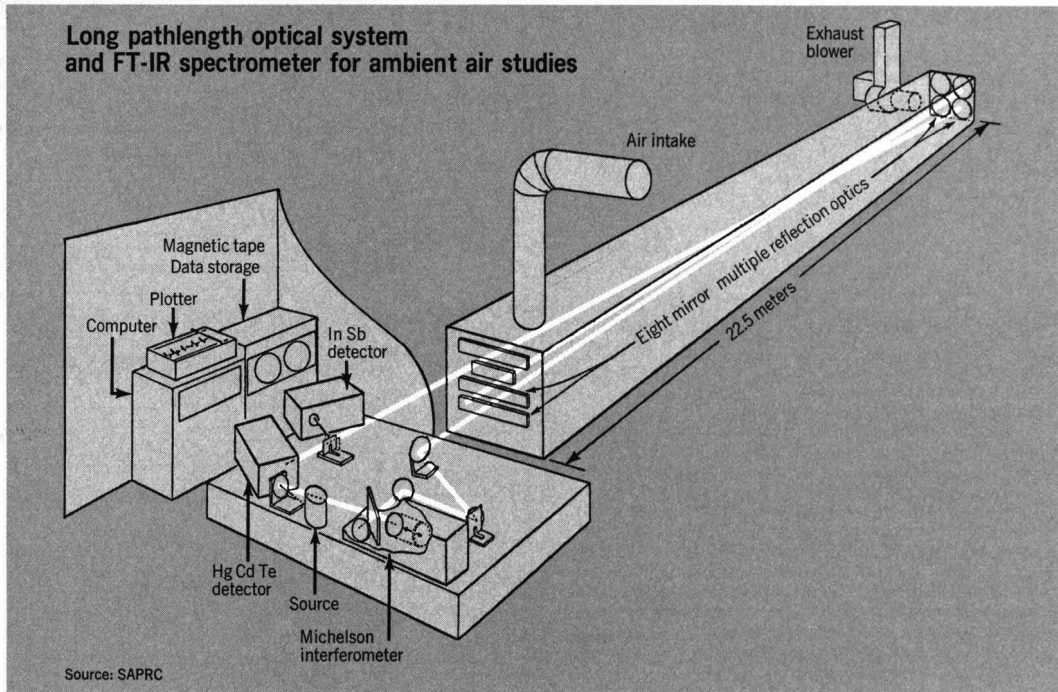


radical (OH), the key species responsible for initiating the free radical oxidation of hydrocarbons, and indeed most organics, in the natural and polluted troposphere. Sources of ambient OH include:

- the reaction of electronically excited oxygen atoms, O (¹D), with water
- the reaction of NO with the hydroperoxyl radical (HO₂)
- the photolyses of nitrous acid (HONO) and hydrogen peroxide (H₂O₂) by solar UV radiation.

The role of ambient OH was suggested by Leighton almost two decades ago, and confirmed by indirect, though convincing, kinetic evidence acquired in laboratory systems over the last 10 years. Only recently, the first direct determination of OH in ambient air was reported by Wang, Niki, Weinstock, and co-workers at Ford Motor Company. Subsequently, Davis et al., then at the University of Maryland, did the first measurements of OH con-

Long pathlength optical system and FT-IR spectrometer for ambient air studies



Source: SAPRC

centrations in the troposphere as a function of location and altitude by using an aircraft as the instrument platform.

While differing somewhat in approach and detail, both of these research teams used tunable UV dye laser systems to monitor OH radicals by their resonance fluorescence. The dye laser was directed into ambient air samples and tuned across a region centered at 282.6 nm, a wavelength that is absorbed by the OH present. A small fraction of the electronically excited OH radicals thus generated return to the ground state by emitting fluorescence, which is detected at 309 nm.

The magnitude of this signal, when corrected for background, is a direct measure of the ambient OH concentration which in the initial experiments ranged from 10^6 – 10^7 radicals/cm³. Such concentrations are consistent with the observed rates of hydration decay (owing to OH attack) in smog chambers (*ES&T*, July 1976, p 692) and in the atmosphere (*ES&T*, March 1976, p 256), as well as with levels predicted by computer modeling studies.

Laser magnetic resonance

Techniques for the detection of radicals such as HO₂ and RO₂ under atmospheric conditions have not yet been developed. Nevertheless, several detection methods have been successfully applied in laboratory studies where these radicals are present at much higher concentrations and in simpler systems than the atmosphere. For example, laser magnetic resonance has been applied by Howard and Evensen of the NOAA Laboratories to kinetic studies of OH, HO₂, and other free radicals, and Radford and Russell have observed the methoxy radical (CH₃O) by this technique.

In these studies, absorption of laser radiation in the far infrared results in transitions between rotational energy levels, which have been brought into resonance by application of a magnetic field. This method affords high sensitivity for free radicals and when combined with a discharge flow system, for example, offers a direct and powerful method for determining absolute reaction rate constants of these radicals with a variety of atmospherically important species.

HO₂, in particular, is a species whose kinetics are notoriously

difficult to study; laser magnetic resonance is one of the few direct techniques available for such studies. However, while such laboratory detection methods for free radicals may ultimately prove adaptable to ambient conditions, the stringent requirements of high sensitivity and specificity, in the presence of a host of other pollutants, may preclude their successful application in atmospheric systems in the near future.

Modes of photodecomposition

The high power and monochromaticity of lasers have also made them valuable in studying the modes of photodecomposition of primary and secondary pollutants under solar irradiation. For example, ozone in the troposphere is important not only because of its impact on human health and on agriculture, but also because upon absorption of actinic ultraviolet light ($290 < \lambda < 400$ nm) it photodissociates into molecular oxygen plus an oxygen atom.

If the light is sufficiently energetic ($\lambda \leq 318$ nm), the oxygen atom can be produced in an electronically excited state, O(¹D); a certain fraction of the O(¹D) atoms then react with water vapor to form OH radicals. While the wavelength dependence of the quantum yield for O(¹D) and, in particular, the precise onset for its production (an important input into chemical models of the stratosphere as well as the troposphere) were in dispute for some years, the use of tunable laser radiation with narrow linewidths has now clarified the wavelength dependence.

Tunable UV lasers also have been useful in elucidating the photochemistry of formaldehyde (HCHO), a key photoinitiator of oxidant. Upon absorbing UV radiation, formaldehyde dissociates by two competing paths, to H + HCO and to H₂ + CO. The free radicals H and HCO react with molecular oxygen to produce HO₂, which is very important in initiating and propagating oxidation chain reactions in smog. In addition, it is speculated that HCO₃ may be formed and may then abstract hydrogen atoms from organics to form formic acid (HCOOH), which has been observed in both laboratory studies and ambient air.

Unfortunately, the results of a number of earlier laboratory studies of the photolysis of formaldehyde were in severe disagreement with respect to the relative, as well as absolute,

quantum yields for the free radical and molecular processes. Recently, however, several laboratories, including that of Lee at UC Irvine, and that of Moore at UC Berkeley, have employed tunable UV dye lasers as light sources to establish the quantum yields for free radical formation as a function of wavelength. Nevertheless, the wavelength dependence of the absolute quantum yields in air and at formaldehyde concentrations in the ppm range remains to be established. Such data are urgently needed since a total pressure of one atmosphere and large quantities of O₂ may well alter the photochemistry from that reported for "laboratory" systems with significantly different conditions.

Long pathlength optical systems

Having considered the application of lasers to the detection of free radicals and to the photodecomposition of some key pollutants, we now consider techniques used for the identification and measurement of a number of noncriteria, labile molecular species. Such compounds generally exist in the atmosphere at ppb concentrations and may be destroyed by conventional sampling and analytical techniques. Therefore, in-situ physical techniques such as absorption spectroscopy must be used for their identification and measurement. In such systems, long optical pathlengths are used in conjunction with high resolution spectrometers. The development of Fourier transform infrared systems has had a particularly significant impact on the application of infrared spectroscopy to atmospheric studies, and we shall emphasize this productive new area.

The magnitude of the infrared absorption of a species is proportional to the concentration of that species in a sample, the pathlength of the infrared beam through the sample, and the inherent absorption strength of the species (as well as the resolution and sensitivity of the detection system). In order to detect ppb concentrations of secondary pollutants by infrared absorption in either laboratory studies or in the atmosphere, a long optical path is required. In contrast to the 10-cm-pathlength cells routinely used in laboratory gas-phase infrared analyses, optical systems with pathlengths of tens, hundreds, or even thousands of meters are used in studies of simulated or real atmospheres.

Pioneering applications of the LPIR (longpath infrared) technique to air pollution research were first done by Stephens and Hanst, Schuck and Doyle, and Calvert and their co-workers in the mid-1950s. They used relatively low resolution prism infrared spectrophotometers and multiple reflection cells giving total pathlengths of 40 to 400 meters. Using this technique, in 1956,

Stephens and Hanst reported the first spectroscopic proof of the presence of ozone in photochemical smog. Shortly thereafter, using this technique, they and their colleagues discovered the highly toxic secondary pollutant, peroxyacetyl nitrate (PAN). Interestingly, this compound was unknown to chemists prior to its characterization in photochemical smog.

FT-IR spectroscopy

The recent availability of commercial Fourier transform infrared (FT-IR) spectrometers with Michelson interferometers and computer data systems had led to significant improvements in sensitivity and spectral resolution, thus enabling further progress to be made in the identification and measurement of labile species in ambient air. FT-IR systems are compared in a general fashion to prism and grating spectrophotometers in Table 1.

Interferometers, the advantages

The fundamental advantage of an interferometer (known as Fellgett's advantage) over a scanning monochromator is that it gathers information at all frequencies in the infrared spectrum simultaneously. Hence, a single interferogram covering 2.5 to 15 μm can be recorded in a few seconds compared to tens of minutes to several hours for a dispersive spectrometer run at equivalent spectral resolution. An important practical aspect of such rapid-scan times and large wavelength range per scan of the interferometer is the ability to determine time concentration profiles (based on simultaneous data points) for a large number of species in a single experiment.

A second important advantage (Jacquinot's advantage) is the improvement in the optical throughput. Whereas radiation reaching the detector of a dispersive spectrometer is attenuated by the entrance and exit slits of the monochromator, which must be very narrow for high resolution spectra, there is no such limitation in an interferometer, except the size of the mirrors.

A third advantage (Connes' advantage) is the accuracy of the frequency determination made possible by the use of the He-Ne laser interferometer to reference the position of the moving mirror.

Present interferometers, using high quality mirror drives, moving over distances of up to 8 cm, and state-of-the-art beam splitters, can routinely achieve 0.0625 cm^{-1} spectral resolution, about 100 times better than possible with the earlier prism spectrometers and about an order of magnitude better than most grating instruments.

The use of a data system for signal averaging and for conducting the fast Fourier transform (or FFT) of the interferogram

TABLE 1.
Comparison of dispersive and FT-IR spectrometers^a

Instrument	Approximate range of spectral resolution ^b (cm ⁻¹)	Scan time	Minimum detectable absorption ln(I ₀ /I)	Frequency calibration	Data handling and presentation	Cost
Prism Spectrophotometer	2-10	Minutes/hours	0.01	External: Reference gases	Recorder tracings of spectra	≥\$7000 ^c
Grating Spectrophotometer	0.5-5	Minutes/hours	0.005-0.01	External: Reference gases	Recorder tracings of spectra; limited data manipulation with computer compatible models	\$5000-30 000
Michelson Interferometer and Data System	0.06-8	Seconds/minutes	0.0005-0.001	Internal: He-Ne laser frequency	Digital processing, storage of completed spectra, wide flexibility in graphical presentations	\$50 000-100 000

^a Values given are averages applicable to a wide range of commercial instruments.

^b Resolution for prism and grating instruments depends upon slit setting and varies with spectral region; resolution for the interferometer is constant throughout the spectral region and depends only upon the length of mirror travel.

^c Prism spectrophotometers have been largely discontinued by major instrument manufacturers within the last two years.

allows on-line data processing. After the interferogram has been transformed, the spectrum is stored in a digital form; this may be further processed and manipulated by using the same computer. For example, subtraction, addition, ratioing, expansion or contraction, smoothing, and other manipulation of spectra (such as degrading resolution to improve apparent signal-to-noise) become more or less routine with the appropriate computer software.

The disadvantages associated with the use of FT-IR spectrometers are their considerably greater complexity compared to prism or grating instruments, the required access to complex facilities, and the comparatively high cost associated with the interferometer and data system.

Ambient air studies

One of the first applications of FT-IR spectroscopy to ambient air analysis was in Pasadena, Calif. in 1973 by Hanst and co-workers. A novel result of these studies was the spectroscopic detection and measurement of relatively high concentrations of formic acid during a severe photochemical smog episode. This observation clearly has interesting mechanistic and health implications.

In the summer of 1976, in collaboration with Hanst, these initial studies of ambient air were extended at the University of California Statewide Air Pollution Research Center (SAPRC) at Riverside to higher sensitivities by using an eight-mirror, 22.5-meter base-path FT-IR and optical paths greater than 1 km. At such pathlengths, owing to the strong absorptions of atmospheric H₂O and CO₂, the spectral windows for infrared detection are generally limited to the 760–1300 cm⁻¹, 2000–2230 cm⁻¹, and 2390–3000 cm⁻¹ regions. This means that some characteristic functional-group absorptions, such as those caused by stretches of the C=O, C=C, and OH bonds, generally cannot be used. Fortunately, however, the majority of pollutant molecules have "fingerprint" absorptions in the accessible infrared regions. In addition, the ambient air spectra can be ratioed against a "clean air" background spectrum with the same water content to eliminate the majority of interfering water absorptions and to facilitate the measurement of band intensities.

At the 0.5 cm⁻¹ resolution routinely used, the vibrational-rotational structure of most light molecules present in the atmospheric sample can be resolved and used for positive identification. Three complete spectra (600–4000 cm⁻¹) can be recorded during each hour, including data collection with 40 scans co-added to enhance the signal-to-noise ratio, routine plotting of a portion of the spectra, and magnetic tape storage. Detection limits, based on a signal-to-noise ratio of 2 in the ratioed spectra, are shown in Table 2 for a number of important pollutants.

In the 1976 SAPRC study, formic acid was again identified in a photochemical smog episode with concentrations ranging from 4–19 ppb. Furthermore, its potential precursor and a known eye irritant, formaldehyde, was also observed at concentrations up to 8 ppb in ambient air spectra recorded after a smog front with ambient ozone levels of 210 ppb moved in.

Nitric acid (HNO₃) is also of interest because of its postulated role in the formation of particulate nitrates. While its vapor pressure is too high to exist as an aerosol, the reaction of HNO₃ with ammonia may be very important in the formation of ammonium nitrate aerosols. This hypothesis was supported in the 1976 Riverside FT-IR study by the observation that the intensity of the HNO₃ spectral features generally decreased when those of ammonia increased. Measurement of HNO₃ in this study was the first spectroscopic observation of nitric acid in a polluted urban atmosphere.

Because of its role in particulate formation, characterization of sources and ambient concentrations of ammonia (NH₃) in the ppb range by FT-IR is also of interest. In the eastern end of California's South Coast Air Basin, for example, which is downwind from various sources of NH₃, levels of particulate nitrate as high as 84 μg/m³ (24-h average) were recorded by SAPRC researchers in February 1977.

Since semicontinuous methods for the analysis of ppb concentrations of NH₃ have only recently been proposed, quantitative determination of NH₃ in the FT-IR facility was of interest. In the Riverside study, NH₃ concentrations ranging from 2 ppb (the detection limit) to 50 ppb were observed.

Nitrous acid, which as noted earlier is a potential source of OH, has not yet been spectroscopically identified in ambient air. However, HONO has been observed in smog-chamber and laboratory studies with FT-IR. Calvert and Shaw and co-workers have applied the FT-IR technique to an investigation of the rates of formation and decay of HONO. Confirmation of the existence of this species in ambient air and determination of its concentrations would be of great value in defining the relative contributions of various sources to the levels of ambient OH as well as in computer modeling of the chemistry of urban atmospheres.

Smog-chamber and lab studies

The short scan times and large wave number range per scan of the interferometer make it an ideal tool for determining time-concentration profiles for a large number of key species in smog-chamber experiments that cannot be measured by conventional monitoring instruments. In the past, product analyses of such experiments have often exhibited poor nitrogen and carbon balances, indicating that substantial quantities of products were not being identified. This limits attempts to characterize the mechanisms of photooxidation of various hydrocarbon-NO_x systems, and becomes critical when such smog-chamber data are used for the purpose of validating computer kinetic models of photochemical air pollution.

In-situ FT-IR spectroscopy can contribute to improved N- and C-balance in chamber experiments. For example, spectra were obtained with an interferometer interfaced to a multiple-reflection cell in the SAPRC 5800-liter evacuable smog chamber during an experiment in which a mixture of propylene, NO, and NO₂ in air were irradiated with a 25-kilowatt solar simulator.

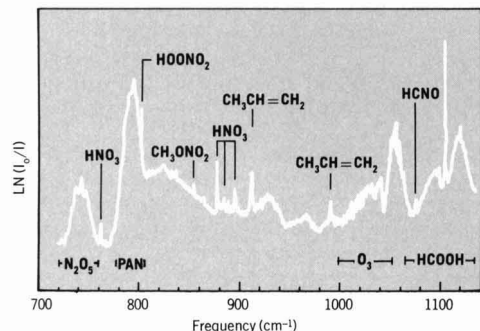
A high-resolution (0.125 cm⁻¹) spectrum from this run contains quantitative information about four species not normally monitored in smog-chamber studies (N₂O₅, HNO₃, HOONO₂, and HCOOH), and a fifth (HCHO) that is generally monitored by a notoriously unreliable wet-chemical method. The observation

TABLE 2.
Detection limits for air pollutants^a

Compound	Measurement frequency (cm ⁻¹)	Detection limit for present system (ppb)
Ammonia	931	2
	967.5	2
Formaldehyde	2779	4
	2781.5	4
Formic acid	1105.3	4
Nitric acid	896	4
Nitrous acid	853 (cis)	4
Peroxy nitric acid	803	4
Nitrogen pentoxide	740	2
	1248	2
Ozone	1055	10
PAN	793	4
	1162	3
Hydrogen peroxide	1250	8
Methanol	1033	2
Methyl nitrate	853	2

^a Using a 1 km FT-IR system

FT-IR spectroscopy detects labile species and improves the nitrogen and carbon balance in smog chamber studies^a



^aPathlength, 85m; Irradiated propene-NO_x air mixture

and quantitative determination (with a time resolution of several minutes during a multi-hour irradiation) of these species exemplifies the dramatic enhancement of chemical information afforded by the FT-IR technique, and has allowed far better mass balances—approaching 100%—to be obtained.

In fact, in analogous FT-IR studies the formation of peroxyacetic acid (HOONO₂) was first discovered in 1976 by Niki and co-workers and independently by Hanst et al. Until that time, the generation of peroxyacetic acid under atmospheric conditions had not been generally anticipated. However, a search for the formation of peroxyformyl nitrate (HCO₃NO₂) in the HCHO-Cl₂-NO_x-air system led to the observation of a series of infrared-absorption bands that were not entirely consistent with those expected for HCO₃NO₂. These bands were subsequently assigned to peroxyacetic acid when they were also observed during photolysis of H₂-Cl₂-NO₂-air mixtures, in which peroxyformyl nitrate could not be formed.

Formation of HOONO₂ by reaction of HO₂ with NO₂ in systems such as these is plausible both thermodynamically and kinetically. While it has been suggested that the rate of formation of HOONO₂ could be as large as that of peroxyacetyl nitrate (PAN), the less stable nature of HOONO₂ suggests that only low concentrations of HOONO₂, relative to a compound such as PAN, should be expected under ambient conditions. However, the discovery in the laboratory of HOONO₂ by FT-IR spectroscopy has spurred a search for it in ambient air.

In-situ techniques such as FT-IR have proven invaluable in studying olefin oxidation reactions since many of the oxidation products are destroyed by more conventional sampling and analyses. Olefin hydrocarbons are thought to be oxidized in ambient air by OH, O₃, and, because of their very low concentrations, to a much lesser extent by oxygen atoms. While many of the mechanistic details of the reactions, especially of OH and O₃, remain to be worked out, it appears that the potential products may include such labile species as hydroperoxides, secondary ozonides, and in some cases, ketene. Such organic acids as formic acid may also be formed.

Gas phase ozone-olefin reactions, for example, were originally thought to produce secondary ozonides in a manner somewhat analogous to the liquid phase reaction. Indeed, such ozonides were observed by longpath infrared spectroscopy almost two decades ago in the gas phase reactions of olefins containing six or more carbon atoms with O₃. Only recently have such ozonides been observed in the reactions of smaller olefins by Niki and co-workers using FT-IR spectroscopy.

This FT-IR technique is also being used to search for the formation of labile and surface-sensitive hydroperoxides in these reactions since thermodynamic studies by O'Neal several years

ago indicated that they may be reaction products. Identification of labile species in such relatively simple systems will potentially provide additional clues as to what to look for in ambient air studies.

The further development and application of high resolution and longpath spectroscopic techniques to the determination of the concentrations and reactions of other highly reactive trace species will undoubtedly lead to significantly improved kinetic computer models for photochemical air pollution, and provide a better means of assessing possible health effects of the spectrum of pollutants present in photochemical smog.

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Additional reading

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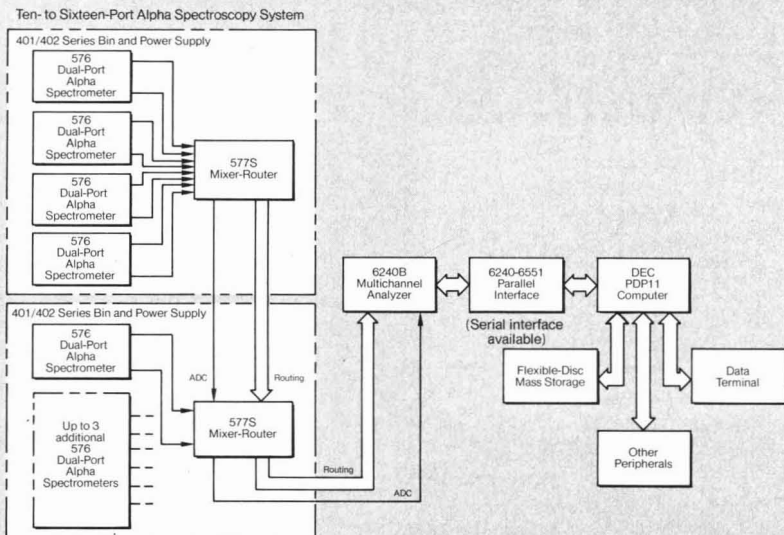
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Determination of Dimethylnitrosamine in Air and Water by Thermal Energy Analysis: Validation of Analytical Procedures

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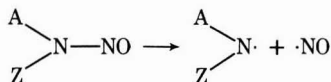
Eugene Sawicki and Ken Krost

Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, N.C. 27711

■ Analytical techniques for the analysis of dimethylnitrosamine (DMN), sensitive at the 1 ng/m³ level in air and at the 2 ng/L level in water, are described. For air analyses, DMN is scrubbed by one of three parallel procedures, cryogenic trapping, trapping in dilute alkali, or trapping on Tenax GC material. To ensure that the analytical procedures are valid and that there is no possibility of a positive or negative interference during scrubbing or subsequent work-up and chromatography, extensive control experiments are carried out on the site of two chemical factories.

Because dimethylnitrosamine (DMN) is a potent carcinogen (1, 2), its presence in air at even the 1000 ng/m³ level may prove to be of concern. Great care is required during sample collection and subsequent analysis to ensure that the DMN being detected has not been formed as a consequence of its being analyzed. DMN was recently reported to be present as an air pollutant in Belle, W. Va., and in Baltimore, Md. (3, 4), and as a water pollutant in Baltimore (5). We report here on the validation of the experimental procedures which were used for the determination of DMN in community air and in drinking water.

The development of a N-nitroso compound specific Thermal Energy Analyzer (TEA) has greatly simplified the analytical techniques because virtually no cleanup or concentration is required (6, 7). With a selective catalyst the TEA pyrolyzer selectively cleaves N-nitroso compounds, splitting off the nitrosyl radical:



where A and Z may be any organic radical. The pyrolysis products then pass through a cold trap held at -150 °C, which freezes out the solvent together with the organic fragments. The nitrosyl radical passes through the cold trap unchanged, after which it is allowed to react with ozone, giving electronically excited nitrogen dioxide. The excited nitrogen dioxide rapidly relaxes to its ground state with the emission of light in the near infrared region of the spectrum. The emitted light is monitored by means of an infrared-sensitive photomultiplier tube, the intensity of the emission being proportional to the number of nitrosyl radicals present. The TEA has been shown to be uniquely selective to the nitroso functional group in both volatile and nonvolatile N-nitroso compounds. In addition, TEA is sensitive to picogram quantities (6) with a

linear response extending over five orders of magnitude. The TEA has been interfaced to both a gas chromatograph, TEA-GC (6), and more recently to a high-performance liquid chromatograph, TEA-HPLC (8).

Experimental

Apparatus. For the analysis of air samples, the air sampling train was mounted inside a mobile, self-contained laboratory. Sample collection, work-up, and analysis were carried out on site in the mobile laboratory. A Thermal Energy Analyzer (Thermo Electron Corp., Waltham, Mass., Model 502), specially modified for field use, was used as the detector for an isothermal single-column gas chromatograph. The gas chromatograph column was prepared from a 6.5 m × 2 mm i.d. stainless-steel tube packed with 15% FFAP on Chromasorb W (acid washed, DCMS treated, 80-100 mesh) and conditioned for 36 h at 220 °C. Argon was used as the carrier gas at a flow rate of 10-30 mL/min. The TEA cold trap was maintained at -79 °C (dichloromethane-dry ice).

Water samples were analyzed on similar TEA-GC equipment located at the Research Center. For analysis of water samples, the TEA cold trap was maintained at -150 °C.

The high-performance liquid chromatograph was constructed by combining a Waters Associates (Milford, Mass.) Model 6000 high-pressure pump with a Waters Associates Model U6K injector. The liquid chromatograph was interfaced directly to the TEA. The TEA-HPLC was operated isocratically with a 30-cm-long, 4-mm-i.d. μ Porasil or a μ Bondapak CN column (Waters Associates). For the μ Porasil, the solvent system was a mixture containing 5% acetone and 95% isooctane at a flow rate of 2 mL/min; for the μ Bondapak CN column, the solvent system was 1.5% acetonitrile and 98.5% isooctane at a flow rate of 1.5 mL/min.

Materials. AnalaR grade acetone, acetonitrile, dichloromethane, and isooctane, which had been distilled from glass, were used. AnalaR KOH was used in the cold traps. Low-temperature slush baths were made with technical grade solvents, maintained at their freezing point.

Procedure. Two different procedures were evaluated for air monitoring. In the first, air was sampled through two successive cold traps, each containing 1 mL of 1 N KOH. The temperature of the two cold traps was maintained at -79 to -95 °C. In the second, air was sampled through an ambient temperature trap containing 50 mL of 1 N KOH. The air flow for both procedures was about 2 L/min and was measured with a mass flow meter (Hastings Model ALL 10K). Air samples were collected over a 30-60-min period, with the total volume of air per sample being about 120 L. After collection the traps

plus interconnecting tube were washed with distilled water. The combined washings were made up to 60 mL and then extracted three times with 8 mL each of dichloromethane. The combined dichloromethane extracts were concentrated on a Kuderna Danish evaporator to a final volume of between 0.4 and 0.8 mL. The temperature of the Kuderna Danish was maintained at 58–60 °C and contained 0.5 mL of isooctane as a keeper. Twenty microliters of the final concentrate was introduced into the TEA–GC and/or the TEA–HPLC.

Water samples were collected in brown bottles and stored at 4 °C. Water (500 mL) was extracted three times with 50 mL of dichloromethane. The combined extracts were dried over 75 g of sodium sulfate. The sodium sulfate was extracted twice with 35 mL of dichloromethane, and the combined dried extracts plus washings were concentrated on a Kuderna–Danish evaporator at 52–53 °C to a final volume of approximately 0.5 mL.

Recovery Experiments

To maximize the usefulness of the mobile air monitoring laboratory, a rapid extraction and concentration procedure was used. Recovery experiments for DMN and other N-nitroso compounds which had been added to the traps were performed daily. By using the same volume of water and dichloromethane for every extraction, the DMN partition between the two solvents was kept constant. Thus, reproducible recoveries were obtained, even though only 8 mL of dichloromethane were used to extract 60 mL of water. By keeping the combined dichloromethane volume to 24 mL, the time necessary to evaporate down to 0.5 mL was kept at a minimum. The recovery of DMN added to the trap was 43.6%, with a standard deviation of $\pm 0.16\%$. The time required for working up an air sample, including chromatography, was less than 90 min.

Extraction of the water samples was carried out at the Research Center, and because rapid analysis time was not essential, more efficient recoveries were obtained than for the air analyses by using larger extraction volumes of dichloromethane. The efficiency of the extraction process was determined by recovery of N-nitroso compounds from water which had been spiked at the 100, 50, and 10 ng/L concentration level. The recovery efficiency ranged from about 68% for DMN to 100% for N-nitroso-sarcosinate (see Table I). Figure 1 is the TEA–GC chromatogram for 25 μL of the dichloromethane extract from a water sample which had been spiked at the 10 ng/L level with DMN, diethylnitrosamine (DEN), dipropyl-nitrosamine (DPN), dibutylnitrosamine (DBN), and N-nitrososarcosinate (SARCOSIN). For most compounds the peaks are clearly discernible, the detection limit for DMN and DEN being about 2 ng/L.

Validation of Procedures

Air Analyses—Cryogenic Trapping. The possibility of DMN being formed as an artifact of the cryogenic collection and TEA–GC measurement technique itself was investigated. In laboratory experiments, dimethylamine hydrochloride and sodium nitrite, each at the 10 ppm (weight to weight) concentration level, were added to the traps. Laboratory air, 120 L, which had been shown to be free of DMN up to the sensitivity limit of the technique, was drawn through the traps. The traps were then extracted and analyzed, and DMN was not found to be present. All samples of dimethylamine or dimethylamine hydrochloride which we have tested contained trace (less than 5 ppm) levels of DMN. The results quoted here have been corrected for DMN which is present in the parent amine.

Because of the possibility that there may be an unknown catalyst in factory and urban air which greatly accelerates the nitrosation reaction, further experiments were conducted on

the site of a chemical factory which was manufacturing unsymmetrical dimethyl hydrazine (UDMH) for which DMN was used as a precursor. Two series of traps were set up side by side, with each series operating over the identical time period. In one set of experiments, conventional traps were set up together with traps to which dimethylamine hydrochloride had been added at a concentration sufficient to produce 100 000 more DMN than was present in the air. The results, shown in Table II, confirm that to within the limits of experimental error, there was no conversion of amine to nitrosamine during collection, extraction, or concentration. In a second set of experiments, conventional traps were set up together with traps containing hydrochloric acid and sodium nitrite. After collection, these traps were thawed and analyzed and again found to contain no excess DMN above that present in the air (Table III). It may be concluded from this experiment that the UDMH factory air contains little if any nitrosatable amine.

Artifact formation during extraction, work-up, and concentration was eliminated as a possibility by conducting the following experiments with the TEA–GC on the site of the UDMH facility. A special air injection inlet system was constructed so that frozen air samples could be analyzed directly without extraction or concentration. The apparatus is shown diagrammatically in Figure 2. From 1 to 5 L of air were pumped through the stainless steel loop held at -79 °C. Water vapor and most organic compounds present in the air were frozen out inside the cold loop. After collection the valve was switched so that argon carrier gas was allowed to sweep through the loop and into the TEA–GC. After purging with

Table I. Recovery Efficiency of N-Nitroso Compounds from Water (10–100 ng/L Level)

Compound	Recovery efficiency, %
Dimethylnitrosamine	68
Diethylnitrosamine	88
Dipropylnitrosamine	94
Dibutylnitrosamine	98
N-Nitrosopiperidine	100
N-Nitrososarcosinate	100
N-Nitrosoatrazine	95

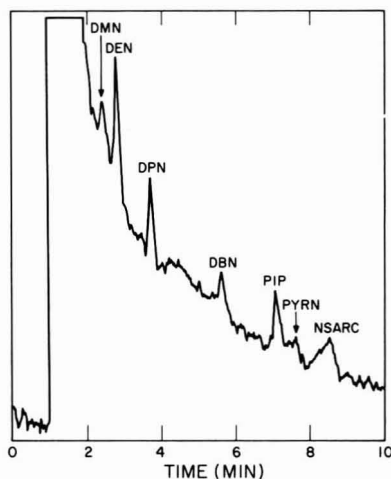


Figure 1. TEA–GC chromatogram of 10 μL of dichloromethane extract following recovery of 0.010 $\mu\text{g/L}$ each of mixture of seven N-nitroso compounds

argon for 2 min, the cold loop was flash heated from -79 to 200 °C, causing the contents of the trap, including the trapped water vapor, to be ejected directly onto the GC column. Figure 3 shows two chromatograms taken with the device while in close proximity to the UDMH factory. Figure 3A is the chromatogram of a 3-min, 3-L sample taken upwind on the UDMH factory. Figure 3B was taken a few minutes later downwind of the UDMH factory. The TEA-GC chromatogram clearly shows a single peak corresponding to 2900 ng/m^3 of DMN downwind of the factory. Since solvent extraction and concentration on a Kuderna Danish evaporator were not used, solvent extraction and concentration cannot be responsible for the DMN which was found.

Formation of DMN in the cryogenic traps from gaseous dimethylamine and oxides of nitrogen was further investigated by drawing an air mixture containing NO and NO_2 over a permeation tube containing dimethylamine. The residence time of the NO, NO_2 , and dimethylamine prior to the cold trap was less than 1 s. The NO_x content of the air stream was varied from 30 to 2000 ppb, with the amine concentration being kept constant at 500 ng/m^3 . DMN could not be detected in the traps, even for the highest NO_x concentrations which were used, indicating that conversion of dimethylamine to DMN was less than 0.01%.

Excess ozone in the air stream was found to catalyze the conversion of the dimethylamine to DMN. The ozone was added by a gas-phase titration technique in just sufficient quantity to oxidize some, but not all, of the NO present. For example, ozone was added to an air stream containing 2000 ppb of NO, in sufficient quantity to reduce the NO concentration from 2000 to 1340 ppb. It was assumed that the de-

pleted NO was converted into NO_2 . The NO and NO_2 concentrations were measured before and after the addition of ozone by means of a chemiluminescent NO_x air monitor (Thermo Electron, Model 14B). Thus, in a 45-min moist air sample containing 2000 ppb NO to which ozone had been added, 20% of the $0.24 \text{ } \mu\text{mol}$ of dimethylamine condensed in the trap was converted into DMN. If dry air were used instead, the conversion to DMN increased from 20 to 75%. If moist laboratory air containing 10 ppb of NO and 10 ppb of NO_2 was ozonated, only 1.2% of the $0.24 \text{ } \mu\text{mol}$ of dimethylamine condensed was converted into DMN. Precoating of the trap with dimethylamine did not effect the percentage yield. We speculate that the mechanism of the conversion is by means of an oxide of nitrogen, possibly NO_3 , formed by prior interaction of NO with O_3 . If the air is moist the resultant ice coats the walls of the trap and locks the amine and the nitrosating agent in an ice matrix. In the absence of an ice matrix, the conversion is more efficient.

In the summertime when ozone levels may be appreciable, it may be possible to have enough ozone present in the ambient air to produce an enhanced conversion of dimethylamine in a cryogenic trap. We therefore recommend that if the cryogenic trap is used when appreciable dimethylamine and ozone concentrations are to be expected, then enhancement experiments with gaseous dimethylamine should also be conducted.

Air Analyses—Ambient KOH Trapping. Use of the ambient KOH trap was first reported by Lazaski (9). We evaluated the retention capacity of the trap by spiking it with $600 \text{ } \mu\text{g}$ of DMN and then passing air through it for a period of 120 min; none of the DMN was lost, even if excess NO_x , NO_x plus ozone, or ozone alone was added to the air stream. The efficiency of the ambient KOH trap was evaluated by first bubbling an air stream through an aqueous solution containing varying amounts of DMN. The air stream was then passed through two ambient KOH traps in series. All the DMN was found to be retained in the first trap, with the carrier over into the second trap being less than 1%.

Identical experiments with ozone, as with the cryogenic trap, were conducted with the ambient KOH trap. Conversion in the trap of gaseous dimethylamine to DMN in the presence of ozone was found to be considerably less than for the cryogenic trap.

The ambient KOH trap was further evaluated in the field on a factory site where dimethylamine was being manufactured. Air was sampled over a permeation tube containing deuterated dimethylamine. On no occasion was any trace of deuterated DMN found.

The ambient KOH trap was found to be as reliable as the cryogenic trap during field use, provided only that care was taken to protect it from bright sunlight. Because the ambient KOH trap is less prone to enhancement effects from ozone, it is the preferred technique when appreciable ozone concentrations are to be anticipated.

Air Analyses—Other Techniques. DMN was identified here by both coincidence of retention time and by comparison of the quantitative amount present in both gas chromatography and high-performance liquid chromatography. Coincidence of retention time using gas-liquid chromatography (where the elution order is solubility/vapor pressure-dependent) and high-performance liquid chromatography (where the elution order is polarity-dependent) may be taken as confirmation of identity, particularly because the TEA detector that was used has been shown to be extraordinarily selective to N-nitroso compounds (7, 10). In all cases, only one major peak was found to be present which corresponds in retention time to DMN; furthermore, the quantitative amount of DMN present was always identical by both the TEA-HPLC and TEA-GC techniques.

Table II. Enhancement by Dimethylamine Hydrochloride

Date, 1975	Site	DMN level, ng/m^3	
		Normal trap	DMA HCl added
11-21	UDMH factory	12 000	16 000
11-21	UDMH factory	3 300	3 300
11-24	UDMH factory	1 900	2 100

Table III. Nitrosation of Cold Trap Contents

Date, 1975	Site	DMN level, ng/m^3	
		Normal trap	Nitrosated trap
11-19	UDMH factory	11 000	9 000
11-24	UDMH factory	2 800	2 200
11-24	UDMH factory	5 600	5 100

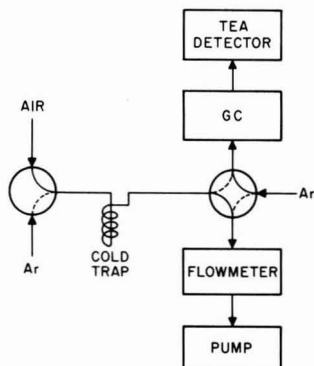


Figure 2. Diagram of apparatus used on site of UDMH factory to demonstrate that observed DMN was not being artifactually produced during dichloromethane extraction and concentration

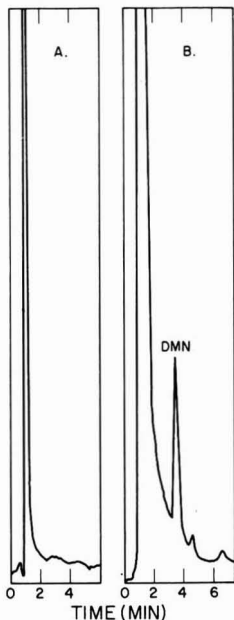


Figure 3. TEA-GC chromatograms taken with apparatus depicted in Figure 1

Three-min, 3-L air samples collected on November 19, 1975, at 10:30 a.m. on site of UDMH factory. Figure 3A taken upwind and Figure 3B downwind of factory

Extensive parallel studies, both in Baltimore and in Belle, were conducted between ourselves and Pellizzari. Instead of trapping the organic vapors cryogenically or in an ambient KOH trap, he concentrated the organics on preconditioned Tenax GC (35/60 mesh) cartridges. The cartridges were desorbed in the laboratory and resolved by capillary gas-liquid chromatography prior to low-resolution mass spectrometry (MS). DMN was unambiguously identified from its mass cracking pattern. In many cases, parallel cryogenic-TEA-GC and Tenax-GC-MS samples were taken at the same day, time, and place. In all cases where parallel sampling was carried out, the results obtained by the two techniques agreed to within the limits of experimental error (11). The possibility of formation of DMN on the Tenax cartridge has also been investigated by Pellizzari both in the laboratory and in the field on the site of the UDMH facility. Enhancement of DMN was not observed when dimethylamine was either preloaded into the Tenax cartridge or when field air was drawn across a permeation tube containing dimethylamine and then into the cartridge.

Finally, further support for the lack of artifactual DMN formation comes from parallel experiments conducted by scientists from the UDMH facility in Baltimore, Md. (12), and a dimethylamine facility in Belle, W.Va. (9). The former group collected samples cryogenically, while the latter group used both cryogenic traps and ambient KOH traps. The samples were extracted with dichloromethane and then chromatographed using GC-MS or GC-Coulson or GC-alkali flame ionization detector instrumentation for final identification. They confirm the presence of DMN in air at concentrations which agree closely with the results presented here.

Water Analyses. The absence of possible artifacts in the extraction process for water analyses was established by the fact that DMN could not be detected when analyzing frozen water to which both sodium nitrite and dimethylamine hy-

drochloride had each been added at the 10–15 $\mu\text{g/L}$ concentration level. Thus, even if free dimethylamine and nitrite had been present in the water, DMN could not have been formed during the extraction, concentration, or chromatography steps. The identity of aquatic DMN was confirmed on several water samples by independent GC-high resolution mass spectrometry (13).

Conclusions

No evidence has been found to suggest that the DMN is being formed as a consequence of being measured, either during collection, concentration, or final quantitation. In the summertime when appreciable ozone concentrations may be expected, great care must be taken to ensure that enhancement is not taking place, particularly if a cryogenic trap is being used.

Acknowledgment

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Determination of Dimethylnitrosamine in Air, Water, and Soil by Thermal Energy Analysis: Measurements in Baltimore, Md.

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■ Dimethylnitrosamine (DMN) is reported to be present as an air pollutant in Baltimore, Md. On the site of a chemical factory that is manufacturing unsymmetrical dimethylhydrazine for which DMN is an intermediate, average DMN levels are 11 600 ng/m³. Average DMN levels in neighboring residential communities are 1070 ng/m³, with DMN levels in downtown Baltimore being between 30 and 100 ng/m³. Salt water from the Curtis Bay and Stonehouse cove area surrounding the chemical factory contains DMN at the 35–940 ng/L level.

Using a new sensitive and selective detector for N-nitrosamines (1, 2), we recently reported dimethylnitrosamine (DMN) to be present as an air pollutant in Baltimore, Md., and Belle, W.Va., at concentrations of between 40 and 300 ng/m³ (3, 4). The presence of DMN in air up to 36 000 ng/m³ has since been confirmed in four independent studies (5–8), including three which used GC–MS techniques for positive identification. Because DMN is a potent carcinogen in laboratory animals, its presence as an air pollutant at concentrations in excess of that of other airborne carcinogens, such as benzo(a)pyrene (9), may be cause for concern.

In Baltimore a source for DMN was traced to a chemical factory that was manufacturing unsymmetrical dimethylhydrazine (UDMH) for which DMN was produced as an intermediate. Because of the data reported here, production of UDMH in Baltimore ceased as of April 1976 (10). This manuscript reports on nitrosamine data, mostly DMN, which were collected in Baltimore during the fall and early winter of 1975, and includes measurements of air, water, and soil, both on and off the UDMH factory site as well as in downtown Baltimore and other areas where the population density is relatively high.

Experimental

Apparatus. For the analysis of air samples, the air sampling train was mounted inside a mobile, self-contained laboratory. Sample collection, work-up, and analysis were carried out on site in the mobile laboratory. A Thermal Energy Analyzer (Thermo Electron Corp., Waltham, Mass., Model 502), specially modified for field use, was used as the detector for an isothermal single-column gas chromatograph. The gas chromatograph column was prepared from a 6.5 × 2 mm i.d. stainless-steel tube packed with 15% FFAP on Chromasorb W (acid washed, DCMS treated, 80–100 mesh) and conditioned for 36 h at 220 °C. Argon was used as the carrier gas at a flow rate of 10–30 mL/min. The TEA cold trap was maintained at –79 °C (dichloromethane–dry ice).

Water samples were analyzed on similar TEA–GC equipment located at the Research Center. For analysis of water samples, the TEA cold trap was maintained at –150 °C.

The high-performance liquid chromatograph was constructed by combining a Waters Associates (Milford, Mass.) Model 6000 high-pressure pump with a Waters Associates Model U6K injector. The liquid chromatograph was interfaced directly to the TEA. The TEA–HPLC was operated

isocratically with a 30-cm-long, 4-mm-i.d. μ Porasil or a μ Bondapak CN column (Waters Associates). For the μ Porasil the solvent system was a mixture containing 5% acetone and 95% isooctane at a flow rate of 2 mL/min; for the μ Bondapak CN column, the solvent system was 1.5% acetonitrile and 98.5% isooctane at a flow rate of 1.5 mL/min.

Materials. AnalaR grade acetone, acetonitrile, dichloromethane, and isooctane, which had been distilled from glass, were used. AnalaR KOH was used in the cold traps. Low-temperature slush baths were made with technical grade solvents maintained at their freezing point.

Procedure. Air samples were collected by flowing 60–120 L of air through two successive cold traps, each containing 1 mL of 1 N KOH. The temperature of the two cold traps was maintained at –79 to –95 °C. After collection the traps plus interconnecting tubing were washed with distilled water. The combined washings were made up to 60 mL and then extracted three times with 8 mL each of dichloromethane. The combined dichloromethane extracts were concentrated on a Kuderna Danish evaporator to a final volume of between 0.4 and 0.8 mL. The temperature of the Kuderna Danish was maintained at 58–60 °C and contained 0.5 mL of isooctane as a keeper. Twenty microliters of the final concentrate was introduced into the TEA–GC and/or the TEA–HPLC.

Water samples were collected in brown bottles and stored at 4 °C. Water (500 mL) was extracted three times with 50 mL of dichloromethane. The combined extracts were dried over 75 g of sodium sulfate. The sodium sulfate was extracted twice with 35 mL of dichloromethane, and the combined dried extracts plus washings were concentrated on a Kuderna–Danish evaporator at 52–53 °C to a final volume of approximately 0.5 mL.

Soil samples were extracted three times with water, and the water in turn was extracted with dichloromethane, as above.

Further details of the analytical techniques, as well as a description of the recovery procedures which were used, and a description of experiments which tested the validity of the procedures are described elsewhere (11).

Results

Figure 1 is the TEA–GC chromatogram of an air sample which was collected on the property of the UDMH facility on November 19, 1975, between 1:50 and 2:50 p.m. The chromatogram shows only two peaks following the solvent front, one corresponding to DMN at the 36 000 ng/m³ level [a parallel Tenax sample (5) which was analyzed by GC–MS and showed 32 000 ng/m³ of DMN] and a smaller peak. The smaller peak elutes close to the retention time of N-nitrosodipropylamine, but its TEA–HPLC retention time is different from that of N-nitrosodipropylamine. The same unknown peak has been observed to be present on several occasions but has not yet been identified. Table I summarizes the data collected on the site of the UDMH factory, close to the dimazine plant. The average DMN level found was 11 600 ng/m³, with the highest value recorded being the 36 000 ng/m³ shown in Figure 1. Two stack measurements were made, one on the

effluent from the dimazine thermal destructor which contained 12 000 ng/m³ of DMN, and the other on the effluent from the wet scrubber which contained 14 000 ng/m³ of DMN.

Table II summarizes data collected within 800 m (½ mile) of the UDMH factory. Three samples taken at the Patapsco Sewage Treatment Plant upwind of the chemical factory did not show DMN to be present, even at the 1 ng/m³ level. A parallel Tenax-GC-MS study also showed DMN to be absent (5). The remaining data points in Table II were all collected at sites downwind of the UDMH factory. The average DMN value found was 1070 ng/m³. Two samples at the Chessie Coal Piers were collected during light rain on October 17, 1975.

Table III shows data collected in the ambient community air of population centers in Baltimore and Arundel County (12). Much of the data presented in this table were taken several miles upwind of the UDMH site. The average DMN

content of the ambient community air of population centers was 100 ng/m³. DMN was found at every site sampled, with the highest level of 760 ng/m³ being recorded on November 25, 1975, near Northbridge Avenue and Cannery Roads in Baltimore.

Drinking water in Baltimore was examined for volatile N-nitrosamines (13), and none was found down to the detection limit of the technique (2 ng/L). Samples of salt water from the estuary comprising the Patapsco River, Curtis Bay, and Stonehouse Cove (see map in Figure 2 and Table IV) were collected and screened for volatile N-nitrosamines. DMN could not be detected in the Patapsco River. The effluent from the sewage treatment plant contained 2 700 ng/L of DMN. At Pennington Avenue one mile south of the UDMH facility, the DMN level in the water was 90 ng/L. At the Chessie Coal Piers southwest of the UDMH facility, the aquatic DMN level was 140–250 ng/L. In Stonehouse Cove immediately adjacent to the UDMH facility, the DMN level in water samples collected from the shore ranged between 260 and 940 ng/L. Water samples from Stonehouse Cove taken both at the surface and at a depth of 6–20 ft all contained DMN. The DMN concentration at the surface was always ½ to ⅓ of that below the surface.

The highest levels of DMN were found at the site of the UDMH factory. A drainage ditch on the east side of the property contained DMN at the 5900 ng/L level. Two mud puddles immediately adjacent to the UDMH factory contained 200 000 and 6 000 000 ng/kg of DMN (moist basis). The concentration levels in the mud puddles are several orders of magnitude larger than previous findings of DMN in the environment. The identity of the DMN in the mud puddle was confirmed by GC-MS.

Discussion

DMN has been shown to be carcinogenic in a wide variety of laboratory animals. For inhalation studies the lowest level tested and shown to be carcinogenic was 200 000 ng/m³ for rats and mice (14). For ingestion studies the lowest level tested and shown to be carcinogenic was 50 000 ng/kg bw/day given to mink, two times per week (15). Factory workers at the UDMH factory were exposed to 8-h average airborne DMN levels of about 11 600 ng/m³. If it is assumed that an average adult takes 16 breaths per minute, with a volume of 0.44 L each, then during the course of an 8-h work day, the adult will have in-

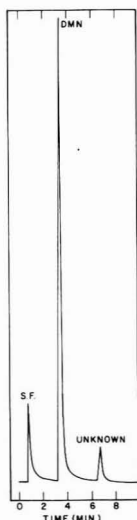


Figure 1. TEA-GC chromatogram following cryogenic trapping, extraction, and concentration taken on property of UDMH facility on November 19, 1975, between 1:50 and 2:50 p.m. DMN present at 36 000 ng/m³ level

Table I. Air Data Collected on Site of UDMH Factory

Date, 1975	Location	Weather		Time, p.m.	DMN, ng/m ³
		Wind	Temp, °F		
11-19	NW of thermal destructor	E, 3 knots	65	1:50-2:50	36 000
11-19	NW of thermal destructor	E, 3 knots	65	3:00-4:00	11 000
11-19	NW of thermal destructor	N, 5 knots	65 clear	4:05-4:25	7 600
11-19	Next to ammonia plant	S, SW, 2	61	5:30-6:30	15 000
11-19	Next to ammonia plant	S, SW, 2	60	6:40-7:40	15 000
11-19	Next to ammonia plant	SW, 3 knots	59	7:40-8:40	30 000
11-19	Next to ammonia plant	SW, W, 3	60	8:40-9:40	8 900
11-19	Next to ammonia plant	Calm	52	9:45-10:45	11 000
11-21	15 ft S of ammonia tanks	N, 5 knots	57	2:15-3:15	12 000
11-21	15 ft S of ammonia tanks	N, NW, 3	51 rain	3:20-4:20	3 300
11-24	S of SE corner of dimazine plant	NE		11:40-12:40	2 800
11-24	S of SE corner of dimazine plant	NE		1:00-2:00	1 900
11-24	S of SE corner of dimazine plant	NE		2:55-3:55	4 500
11-24	S of SE corner of dimazine plant	NE		7:00-8:00	5 500
11-24	S of SE corner of dimazine plant	NE		7:00-8:00	5 600
10-15	E parking lot	W, SW, 10	87	12:17-1:35	13 000
10-15	E parking lot	SW, 10 knots	86	2:30-3:30	15 000
10-15	E parking lot	SW, 9 knots	85	4:15-5:45	11 000
10-15	E parking lot	SW, 5 knots	80	6:00-7:00	8 700
11-24	Thermal destructor stack	NE		4:25-5:00	12 000
11-24	V602 wet scrubber stack	NE		5:50-5:50	14 000

haled 3.3 m³ of air (4). If it is further assumed that the DMN was retained by the body, then a factory worker would have an intake of 39 000 ng of DMN per 8-h day.

Residential communities near the factory were exposed to 24-h average airborne DMN levels of about 1070 ng/m³, corresponding to an intake of about 10 000 ng of DMN per day. Communities upwind and far removed from the factory were exposed to airborne DMN levels of between about 30 and 100 ng/m³ for part of the day, corresponding to a DMN intake of about 300 ng per day. Direct human exposure resulting from the DMN levels in the soil and in the estuary would not be

expected to be significant. By comparison the expected total DMN intake from eating four slices of cooked bacon would be about 500 ng. The total DMN intake from a pack of 20 cigarettes would be about 1000 ng (16). We conclude, therefore, that the daily DMN intake in communities far removed from the factory site was somewhat less than the intake from normal dietary routes. However, communities bordering the factory, and the factory workers themselves, had a DMN intake considerably in excess of that from eating or smoking. The risk to human health of daily DMN intakes of the order of 10 000–30 000 ng per day remains to be assessed.

Table II. DMN in Community Air Within 800 Meters (1/2 mile) of UDMH Factory

Date, 1975	Location	Weather		Temp, ° F	Time, p.m.	DMN, ng/m ³	NO, NO ₂ , ppb
		Wind					
10-16	Patapsco Sewage Plant	N, NW, 9 knots		72	11:10–1:10	ND	15, 15
10-16	Patapsco Sewage Plant	NW, 10 knots		73	1:30–3:30	ND	8, 20
10-16	Patapsco Sewage Plant	NW, 9 knots		72	3:50–5:30	ND	10, 15
10-22	Northbridge Rd				4:10–5:10	1 400	
10-22	Northbridge Rd				8:30–9:30	410	
11-20	Conoco, corner Fairfield and Chesapeake	SW, 6 knots		70	3:45–4:45	340	
11-20	Conoco, corner Fairfield and Chesapeake	Clear					
11-20	Minerac Corp.	SW, 3 knots		61	5:00–6:00	1 800	
11-20	Minerac Corp.	Clear-cloudy					
11-20	Minerac Corp.	S, 4 knots		57	8:20–9:20	170	
11-20	Minerac Corp.	S, 4 knots		57	9:30–10:20	330	
11-22	200 yd, E in B Plot	W, NW 7 knots		49	1:15–2:15	2 200	
11-22	200 yd, E in B Plot	W, NW 7 knots		47	2:15–3:15	3 000	
8-23	Chessie Coal Piers				7:00–9:00	33	
10-17	Chessie Coal Piers	E, NE, 7 knots		56	11:00–1:00	1 800	37, 25
10-17	Chessie Coal Piers	N, NE, 7 knots		56	1:15–3:15	1 200	50, 25
		Rain					
10-17	Chessie Coal Piers	E, 14 knots		56	3:45–5:45	130	37, 50
		Rain					

Table III. DMN Levels in Community Air of Population Centers in Baltimore

Date, 1975	Location	City	Weather		Misc	Time	DMN, ng/m ³
			Wind	Temp, ° F			
11-22	Corner Howard and Preston	Baltimore	Variable, 2 knots	41	Clear	6:42–7:55 a.m.	26
11-22	Corner Pratt and Commerce St.	Baltimore	W, SW, 7 knots	47	Clear	8:25–9:25 a.m.	88
11-22	Corner Pratt and Commerce St.	Baltimore	W, SW, 7 knots	47	Clear	9:25–10:25 a.m.	110
12-14	Corner N Baltimore and W Liberty on W Fairmount Ave.	Baltimore	W, SW, 7 knots		Foggy	6:35–7:05 a.m.	49
12-14	Corner Lombard and Calvert Ave. across News American Bldg	Baltimore		41	Foggy	8:00–9:00 a.m.	48
12-14	Liberty and W Fayette St.	Baltimore	SE, 5–6 knots	42	Fog lifting	9:00–10:00 a.m.	22
12-14	South St. and Pratt St.	Baltimore	S, SW, 6 knots	42	Overcast	10:50–11:35 a.m.	28
12-14	South St. and Pratt St.	Baltimore	S, SW, 6 knots	42	Cloudy	11:00–11:45 a.m.	
12-13	Gov. Ritchie Highway, Brooklyn Park Plaza Shopping Center	Arundel County			Cloudy	3:45–4:54 a.m.	110
12-13	Rt. 2, Gov. Ritchie Highway	Arundel County	E, NE	44	Light rain	5:55–7:13 a.m.	36
12-13	Stahl and Ordnance Rd.	Arundel County	NW	45	Light rain	7:29–8:29 a.m.	31
12-13	Solly School, off Fort Smallwood Rd.	Arundel County		44	Overcast	8:53–9:42 a.m.	23
12-13	Park, W Bay Ave.	Arundel County	N, NE, 10 knots	44	Overcast	10:05–10:50 a.m.	21
12-13	4th and Edison St.	Arundel County		44	Cloudy	11:02–12:35 p.m.	16
12-13	Spruce and Fairhaven Ave.	Arundel/Baltimore		44	Cloudy	2:00–2:45 p.m.	125
12-13	Spruce and Fairhaven Ave.	Arundel/Baltimore			Cloudy	3:00–3:45 p.m.	116
11-25	Northbridge and Cannery Rd.	Baltimore	W, NW, light		Cloudy	12:38–1:38 p.m.	180
11-25	Northbridge and Cannery Rd.	Baltimore	W, NW, light		Overcast	5:00–6:00 p.m.	760
12-11	Cannery, 4th (playground)	Baltimore			Clear, sunny	10:45–11:45 a.m.	212
12-11	Corner Cannery and 4th (playground)	Baltimore			Cloudy	11:58–12:58 p.m.	60
12-11	Corner Cannery and 4th (playground)	Baltimore			Cloudy	1:45–2:45 p.m.	66
12-11	Corner Cannery and 4th (playground)	Baltimore			Cloudy	2:51–3:51 p.m.	57
12-11	Corner Cannery and 4th (playground)	Baltimore			Cloudy	4:00–4:20 p.m.	107
12-15	Corner Cannery and 4th (playground)	Baltimore			Clear	7:37–8:37 a.m.	58
12-15	4th St. and Highland Ave., 4 Corners Rest.	Baltimore	E, light SW	Cold	Clear	12:40–1:40 p.m.	46
12-15	4th St. and Highland Ave.	Baltimore	SW		726 mm Hg	2:32–4:32 p.m.	36
12-15	4th St. and Cannery (playground)	Baltimore				6:55–7:30 p.m.	110

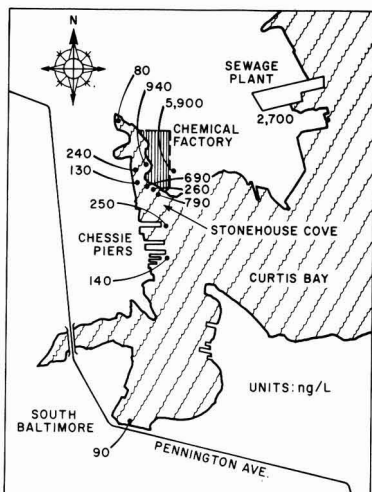


Figure 2. Map of South Baltimore showing location of aquatic DMN

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Table IV. Aquatic DMN

Date, 1975	Description of sample site	DMN, ng/L
11-21	Tap water, Baltimore	N.D. (<2)
11-24	Commercial Wharf, Boston, ocean sample	N.D. (<2)
10-10	Off Pennington Ave., Baltimore	90
10-10	Sewer sample, Baltimore	2 700
10-10	Curtis Bay, near Chessie Piers	240
10-10	Curtis Bay, near Chessie Piers	130
10-17	Chessie Piers	250
10-17	Chessie Piers	140
10-21	Sewer sample, Buck River	N.D. (<50)
11-21	Stonehouse Cove, W of UDMH Facility	940
11-21	Stonehouse Cove, W of UDMH Facility	690
11-21	Stonehouse Cove, S of UDMH Facility	260
11-21	Stonehouse Cove, S of UDMH Facility	790
11-20	Stonehouse Cove, Buoy S "2", Sur.	35
11-20	Stonehouse Cove, Buoy S "2", 20'	140
11-20	Stonehouse Cove, Buoy S "4", Sur.	N.D. (<5)
11-20	Stonehouse Cove, Buoy S "4", 20'	140
11-20	Stonehouse Cove, Buoy N "6", Sur.	56
11-20	Stonehouse Cove, Buoy N "6", 6'	130
11-22	Water drainage ditch, E of UDMH Facility	5 900
11-21	Mud Sample, S of UDMH Facility	200 000
11-21	Mud Puddle, S of UDMH Facility	6 000 000

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Cd Ion Activity in Soils: Evaluation of Cd Ion-Selective Electrode

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■ Cadmium ion activity was measured in 0.05 M $\text{Ca}(\text{NO}_3)_2$ extracts of two soils containing up to 100 ppm Cd. Comparative analyses by atomic absorption spectroscopy showed excellent agreement with the electrode method ($r = 0.99$, $b = 1.03$), suggesting the bulk of soluble Cd in solution was Cd^{2+} ions. Interference phenomena associated with the electrode were characterized. Cleaning the electrode by machine buffing and/or washing in EDTA was necessary for reproducible readings. Interference in soil extracts was primarily due to loosely adsorbed Cd, Pb, Cu, and Zn ions on the electrode surface. The detection limit of the electrode in soil extracts was 0.05 $\mu\text{g Cd/mL}$. The electrode cannot be used for analysis of soils containing highly concentrated Pb^{2+} , Hg^{2+} , Cu^{2+} , or Ag^+ .

Knowledge of the free ion activity of metals is necessary for understanding solid-phase and complexation reactions occurring in soils (1). Presently, the best available method for determining metal ion activity in soil solution is the use of specific ion electrodes.

The Cd ion-selective electrode develops a potential proportional to the logarithm of the activity of the Cd^{2+} ion in solution (2). The electrode response is described by the Nernst equation:

$$E = E_a + \frac{2.3 RT}{2 F} \log A_{\text{Cd}^{2+}} \quad (1)$$

where E = measured potential, E_a = potential due to reference electrodes and extraneous sources, $2.3 RT/2 F$ = Nernst factor, and $A_{\text{Cd}^{2+}}$ = Cd ion activity.

The Nernst factor is represented by the slope in the linear region of the standard curve for the Cd electrode (Figure 1). The ideal slope is a 29.6-mV change in potential per decade change in Cd ion activity at 25 °C.

The Cd-ion-selective electrode is a solid-state membrane of CdS in a matrix of Ag_2S . The response is not completely selective if a matrix of heavy metals exists in the solution being analyzed. Consequently, interferences may be a problem when the electrodes are used to determine ion activity in soils from a polluted environment.

Blaedel and Dinwiddie reported on the behavior of the solid-state Cu electrode in the submicromolar range (10^{-6} – 10^{-9} M Cu ion) and found that cleaning the electrode in dilute H_2SO_4 was necessary for reproducible readings (3). The postulated mechanism of interference was adsorption of Cu ions on the electrode surface which upset the equilibrium with CuS. Slight interference at the 10^{-7} M level of Cu ion was reported with 10^{-5} M concentrations of H^+ , Ca^{2+} , Zn^{2+} , Al^{3+} , and Fe^{3+} . The Cd ion electrode may behave in a similar manner, since both it and the Cu ion electrode are solid-state membrane electrodes of respective sulfides in an Ag_2S matrix.

The Cd ion-selective electrode was used to evaluate the formation of labile Cd complexes in natural waters (4). Experimental samples included borehole water, settled sewage, sewage effluents, and river water. The estimated Cd^{2+} in these samples ranged from 29 to 89% of the total dissolved Cd. The

distribution of the remaining Cd was calculated for CdOH^+ , CdCO_3 , CdCl^+ , CdSO_3 , and a humic complex. There was no attempt to characterize interference by other heavy metals, and cleaning the electrode with acid or chelate solution was not considered.

The Cd ion-selective electrode could be useful for analyzing Cd activity in soil solutions, if the electrode is accurate and free from interferences. The electrode is portable and could be used in the field for preliminary analysis of Cd contamination. However, more understanding of the electrode response to Cd in soil extracts is necessary before such applications are feasible. Therefore, a study was made to test the response of the Cd ion electrode in filtered soil extracts containing 0.05–2 ppm (mg/L) total dissolved Cd, and to characterize interference from other ions in solution. Total Cd determined by atomic absorption spectroscopy was compared to the Cd ion activity determined with the Cd ion electrode.

Methods and Materials

An Orion Model 94-48 Cd ion-selective electrode in conjunction with an Orion Model 90-01 single junction reference electrode was used for all Cd activity measurements. A Corning Model 110 pH meter connected to a Honeywell recorder was used to record the electrode response.

An extracting solution for soils of 0.05 M $\text{Ca}(\text{NO}_3)_2$ was used to blank out the effects of other salts on total solution ionic strength. Standard solutions were also made in 0.05 M $\text{Ca}(\text{NO}_3)_2$ to closely duplicate the ionic strength of the soil extracts.

All standard solutions were prepared from a stock solution of 0.1 M Cd ($\text{NO}_3)_2$. Successive dilutions were made using dilution factors no greater than 100. The diluted solutions were stored in 100-mL polyethylene bottles. A check of the standards by atomic absorption analysis showed all concentrations were stable with respect to time.

Ten separate standard curve determinations were made at various times within a six-month interval (Figure 1). All measurements were made at ambient room temperature (20–25 °C). Temperature effects on the slope of the standard curve were minimized by producing each curve at the same temperature.

The electrode was cleaned after each analysis by immersion into 0.01 M EDTA until the electrode potential was between

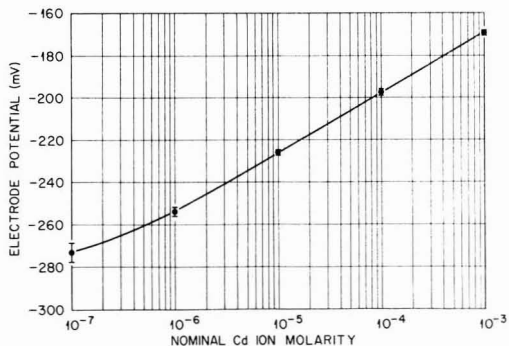


Figure 1. Mean response of Cd ion-selective electrode in standard Cd solutions

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-320 and -330 mV. The cleaning procedure assured that any contamination remaining on the electrode surface would not be transferred to subsequent samples. A motorized cloth buffer unit was used to remove any other contamination. The degree of cleaning required was dependent on the concentration of interfering ions and the time of immersion in solution.

The same 0.01 M EDTA cleaning solution was used to clean the electrode after immersion into several soil extracts. A subsequent analysis of the 0.01 M EDTA solution revealed an enrichment of Cd, Cu, Zn, Fe, and Pb ions in the solution, which indicates that the heavy metals were loosely adsorbed or precipitated on the electrode surface. The exact quantity of adsorbed ions was not determined, but the relative amounts depended on the time of immersion and the ionic character of the solution. Significant interference did not occur when the metal ions were not allowed to accumulate between samples.

Triplicate 10-g samples of Captina and Emory silt loam soils (described in Table I) were treated with Cd(NO₃)₂ at rates of 0, 5, 10, 50, and 100 µg Cd/g soil (air-dry basis). Solutions containing appropriate amounts of Cd in 25 mL of 0.05 M Ca(NO₃)₂ solution were shaken for 16 h with the soil. The suspensions were subsequently filtered through No. 42 Whatman paper prior to analysis by the Cd ion electrode. All filtrates were then analyzed for total Cd by atomic absorption spectroscopy.

Results and Discussion

Response of Electrode to Standard Cd Solutions. The potential of the Cd ion-selective electrode in standard solutions was highly predictable (Figure 1). However, the standard error of mean potentials increased inversely with the concentration of Cd in solution. These results indicate the electrode is less reliable in measuring Cd activity in the range of 10⁻⁷-10⁻⁶ M Cd (0.01-0.11 mg Cd/L).

The time dependence of the electrode response was determined for up to 30 min in Cd ion solutions of 10⁻⁷-10⁻³ M (Figure 2). From these curves an optimum time of 5-10 min was derived for contact of the Cd electrode with the solution. This amount of time was necessary to allow initial equilibration of the electrode with solution and to minimize the electrode drift associated with prolonged contact periods.

Effects of Interfering Ions. The Cd electrode may be deactivated if the sample solution contains ions such as Cu²⁺, Hg²⁺, Pb²⁺, and Ag⁺, which can form a more insoluble sulfide salt than CdS (5). Precipitation of the interfering metal sulfide occurs on the membrane surface and changes the conductive properties of the electrode. Background levels of these metals in the soils used in this study were assumed to be low enough to prevent interference. This assumption may not be valid for the analysis of contaminated samples; a matrix of heavy metals is usually present in soils contaminated from industrial sources (6).

The solubility product constants (-log K₀) for CdS and PbS are reported to be 27.9 and 29.0, respectively (7). When the Pb²⁺ concentration in solution exceeds the solubility level of PbS, Pb²⁺ will precipitate and form PbS on the electrode surface, causing interference. Since the solubility product is near that of CdS, a relatively high concentration of Pb²⁺ can be tolerated. The response of the electrode to Cd²⁺ and Pb²⁺ solutions (Figure 3) was measured to determine the extent of Pb²⁺ interference. In most cases, the Pb²⁺ concentration had to be at least one order of magnitude lower than Cd²⁺ to prevent interference. These results were not consistent with the Cd electrode instruction manual which states that interference does not occur when Pb²⁺ and Cd²⁺ are in equimolar concentrations (8).

Electrode interference due to Pb²⁺ was characterized by

a positive drift occurring immediately after the electrode was immersed in the test solution. The degree of interference was a function of the Pb²⁺ ion concentration and the amount of electrode immersion time.

Comparison of Analysis by Cd Electrode and Atomic Absorption. Results obtained with the Cd electrode are comparable to atomic absorption analysis (Figure 4) except for Emory soil treated with 5 ppm Cd. The Cd concentration of 0.03 mg/L in these solutions was below the detection limit of 0.05 mg/L imposed on the Cd electrode. This point was excluded from the regression analysis. The following regression equation was fitted to the remaining points:

$$\log Y = 1.03 \log X + 0.094 \quad (2)$$

where Y = Cd (ppm) by atomic absorption analysis, and X = Cd (ppm) by Cd electrode analysis.

The regression equation represents a simple technique to quantitatively compare the two methods over three orders of

Table I. Chemical and Physical Characteristics of Experimental Soils

Soil	pH	CEC, meq/100 g	OM, %	Clay, %	Silt, %	Sand, %
Emory silt loam	5.5	10.6	4.7	14.8	58.6	13.6
Captina silt loam	5.6	8.5	3.2	63.7	29.1	7.2

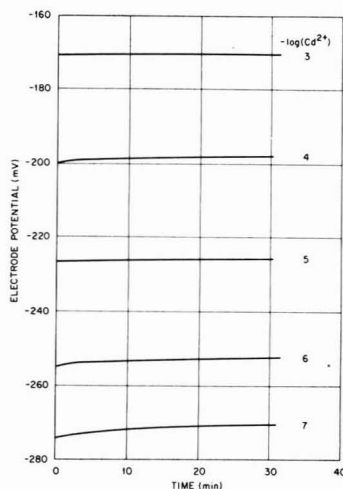


Figure 2. Dependence of electrode response on time of immersion in standard Cd solutions

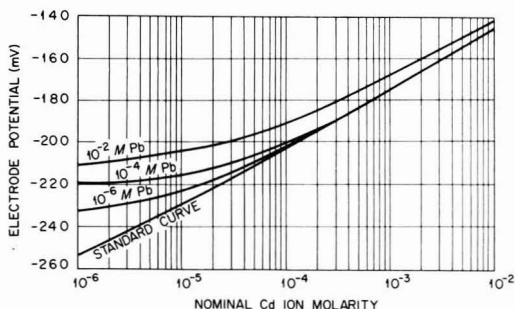


Figure 3. Effect of Pb ion on response of Cd ion-selective electrode in standard Cd solutions

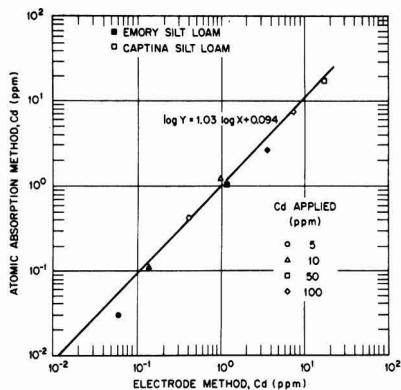


Figure 4. Comparison between atomic absorption and Cd electrode analysis of extracts from two soils containing up to 100 ppm Cd

magnitude of Cd concentration. Excellent agreement was found between the two methods ($r = 0.998$, $b = 1.03 \pm 0.04$), and the regression coefficient of 1.03 is within one standard deviation of the expected value of one.

Complete agreement between the two methods of analysis is expected only when the total dissolved Cd within the soil extracts is in the Cd^{2+} form ($b = 1.00$). Studies on soil extracts have verified that Cd forms only weak complexes with soluble soil organic matter (Bondietti, unpublished data). The possibility of Cd being involved in ion pair formation was ruled out on the basis of high ionic strength and low formation constants with predominant anions (7). The results of this study strongly indicate that the bulk of dissolved Cd in the tested soils extracts is uncomplexed and in the form of Cd^{2+} .

Summary and Conclusions

The Cd electrode was useful for routine analyses of soil extracts containing greater than 0.05 mg Cd/L. Precautions

were made to prevent interferences by other ions by rinsing the electrode in 0.01 M EDTA, and/or by cleaning the electrode surface with a motorized buffer.

Extracts of two soils treated with 5, 10, 50, and 100 ppm Cd were tested with the Cd electrode, and the results were compared to analysis by atomic absorption. Excellent agreement was found between the two methods ($r = 0.998$, $b = 1.03$). These results indicate that the bulk of the Cd extracted from the two experimental soils was in the form of Cd^{2+} .

The usual presence of a matrix of heavy metals in contaminated soils may limit the utility of the Cd ion electrode. For example, soils heavily contaminated with Pb cannot be analyzed with the electrode unless the concentration of Cd in the extractant solution exceeds that of Pb by at least an order of magnitude.

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Continuous Mass Spectrometric Analysis of Particulates by Use of Surface Ionization

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■ An instrument for real-time analysis of airborne particulates by use of surface ionization is constructed and evaluated. The particles impinge on a heated Re ribbon, and the resulting burst of ions produced by each particle is analyzed in a 3-in. radius magnetic sector mass spectrometer. The ionization efficiency appears to obey the Saha-Langmuir equation. Oxygen in the air raises the work function of the Re to about 7.2 eV at 1000 K allowing analysis of elements with ionization potentials as high as 8 eV. In favorable cases, particles containing 1000 atoms of a particular element and particle concentrations of less than 1 per cm^3 can be detected.

Surface ionization or thermionic emission of ions from a heated surface has long been one of the standard methods used by mass spectroscopists for analyzing very small amounts

of solid material. The sample is placed onto the ionizing filament and on heating the filament, ions and neutrals are emitted according to the Saha-Langmuir equation:

$$\frac{n_+}{n_0} = \frac{g_+ (1 - r_+)}{g_0 (1 - r_0)} \exp\left(\frac{\phi - IP}{RT}\right)$$

where n_+/n_0 is the ratio of positive ions to neutral atoms, ϕ is the work function of the surface, and IP is the ionization potential of the evaporating atom or molecule. g_+/g_0 is the ratio of the statistical weights of the ion and atom and has a value of the order of unity. (For alkali metals, $g_+/g_0 = 1/2$.) The reflection coefficients for ions and neutrals, r_+ and r_0 , are usually small.

To analyze particulates by mass spectrometry, the usual technique is to collect a sample by drawing air through a filter or an impinger for periods of up to 24 h. This technique, of course, has not only the usual problems associated with

transferring the sample to the ionizing filament but also the disadvantage that only an average value for the concentration is obtained. By impinging the air stream directly against a heated ionizing filament, these two disadvantages can be eliminated and at the same time, the added oxygen will tend to adsorb on the filament and increase its work function. The ordinary gaseous components of the air have ionization potentials much too high to be ionized and hence do not present any interference problems. At sufficiently high temperatures, each particle as it hits the filament should produce a burst of ions. The number of ions in the burst should give a measure of the amount of that element in the particle, and the number of bursts per second should be proportional to the number of particles per cm^3 in the air. This report describes the apparatus used to study this technique and the preliminary results obtained for a variety of particles, including natural air particulates.

Apparatus

As can be seen from Figures 1 and 2, the basic ion source and mass spectrometer used in these studies was of conventional design. The unique feature of the equipment lies in the method used to introduce the sample to the heated surface of the ionizer.

As shown in Figure 1, the air sample first passes through a rather crude needle valve which serves to adjust the air flow to the optimum value or to shut off the flow when not needed.

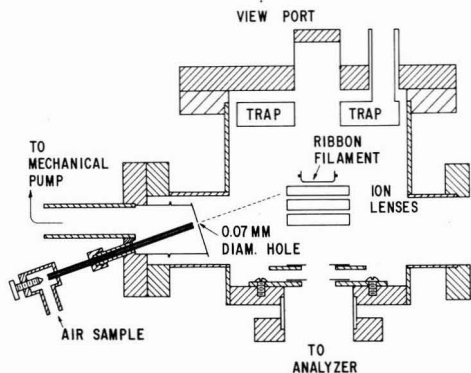


Figure 1. Diagram of sample inlet system and ion source chamber. Empty side port for electrical feedthroughs

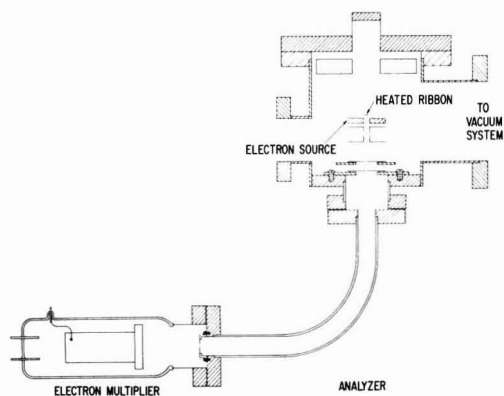


Figure 2. Diagram of complete instrument including mass analyzer. View 90° from Figure 1

The air then travels down about 25 cm of 1.6-mm i.d. stainless steel tubing and impinges on a small hole of about 0.05–0.07 mm diameter. Most of the data reported here were obtained with a 0.071-mm diameter hole produced by a laser in a 0.76-mm thick sheet of stainless steel. Most of the air is removed by a 160 L/min mechanical pump attached to the small chamber shown in the figure. Some of the sample particles and air pass through the hole and impinge on a 3.2 mm \times 19 mm metal ribbon heated directly by an electric current to 600–2000 °C. The ions produced as a particle hits the surface of the ribbon are accelerated and focused by a simple system of three split-plate electrodes and then mass analyzed in the usual manner. Only a simple nondouble-focusing mass analyzer is required to give good mass resolution. The ions are formed with only thermal energy, and hence the energy spread in the ion beam is very low.

The first pair of electrodes also served as an electron bombardment ion source for analyzing the neutral gaseous components present in this region. The doughnut-shaped liquid N_2 trap above the ribbon helped to reduce the partial pressure of organic impurities which produce interfering ion peaks in the mass spectrum. Ordinarily, however, the desired signal was large enough that this trap was not necessary.

The mass spectrometer was a 7.62-cm (3 in.) radius -90° magnetic sector type instrument with entrance and exit slits of 0.254 and 0.381 mm, respectively. At the normal acceleration voltage of 500 V, the resolution was sufficient to separate the mass peaks up to about mass 115 ($M/\Delta M = 115$ for $\Delta M =$ peak width at 10% of peak height). Numerous measurements both with ions from the surface ionization filament and from the electron bombardment source showed that the overall transmission of ions from source to detector was about 4%.

The 10-stage box-and-grid type electron multiplier had a background count rate which varied from 1 to 0.05 ion/s. Because the ion background from the mass spectrometer during operation was usually considerably higher than this value, no effort was made to improve it.

For simplicity, no differential pumping was used in the design of the mass spectrometer; hence, a large pumping speed was required. This was achieved by using a 4-in. oil diffusion pump and liquid nitrogen trap backed by a mechanical pump. The system was normally baked at 300 °C for several hours to reduce the organic background. The pressure after bakeout was typically in the 10^{-9} torr range and consisted mostly of mass 28 (probably CO). However, because of the high ionization efficiency of many organic compounds, the organic peaks in the surface ionization spectrum were never completely eliminated—merely reduced to a tolerable level. In retrospect, a cleaner pumping system would have been desirable. A small Hg diffusion pumped system baked out at 400 °C achieved a considerably cleaner surface ionization spectrum.

In spite of hundreds of hours of use, the Re ribbon was not appreciably affected by the oxidizing atmosphere. At the low temperatures usually used during an analysis, the life should be very long.

Ionization Efficiency

As can be seen from the Saha-Langmuir equation, the ionization efficiency depends strongly on the difference between the ionization potential of the vaporizing atom and the work function of the metal surface. Thus, the success of this method of ionization for high ionization potential elements depends greatly on the choice of metal surface and the increase of the work function of that surface by adsorption of oxygen from the incoming air.

Only two metals, W and Re, have been used in this study. The Re ribbon was fabricated from electron-beam zone re-

fined material. The tungsten ribbon was ordinary type 218 tungsten ribbon which had been repeatedly flashed to 2300 K in high vacuum prior to the measurements. The thickness of the ribbons was 0.030 mm for the Re and 0.015 mm for the W. Ribbon temperature was measured with an optical pyrometer. The initial studies were made with W but Re proved to be greatly superior to W. Most of the data presented here are with the Re ribbon.

The amount of oxygen adsorbed and hence, the increase in the work function, increases with oxygen pressure and decreases with temperature. The pressure of air at the metal surface was limited to the range $1-5 \times 10^{-5}$ torr. The temperature used depended on several factors but was usually a compromise between efficiency of ionization and rate of evaporation of the element from the surface. The temperature term in the Saha-Langmuir equation indicates that the efficiency should increase with temperature, but except for very high temperatures where the oxygen has been completely desorbed or for very low temperatures where the surface is saturated with O_2 , the work function change is the more important parameter. The background of undesired ions also changes with temperature and must be considered when choosing the optimum temperature. For the elements investigated, the optimum temperatures were in the range 800-1500 K.

In situ experimental measurements of the work function of the Re ribbon are shown in Figure 3. The value of 5.4 eV for the clean surface was obtained from the slope of the Richardson plot of the electron emission as a function of temperature in high vacuum. The absolute electron current density also agreed with this value.

This value is higher than the reported value of 5.0 eV for polycrystalline Re (1). However, the basal plane of Re (0001 plane) has been reported to have a work function of 5.59 eV (2). This suggests that the surface of the zone-refined Re filament used in this experiment probably is composed predominantly of the higher work function surfaces. A similar determination of the W ribbon yielded the accepted value of 4.6 eV.

The high-temperature results for oxidized Re (open circles) were obtained by measuring the drop in electron emission on admitting air. The lower temperature values using Pb_3O_4 and $BiCO_3$ particles (squares) were obtained by comparing the integrated output ion currents (Pb^+ or Bi^+) at several temperatures for an unknown but approximately constant dose of dust particles onto the ribbon. The highest temperature used was in the range where the work function was known from the electron emission measurements, and this value then served as the basis for calculating the work functions at lower temperatures.

The solid circles result from an attempt to measure the work function directly by determining the number of ions produced at the ribbon by particles of known size. A monodispersed particle generator would have been desirable for this work but was not available. The particles were obtained by shaking a jar of dust particles of various compounds and allowing the particles to settle for various time intervals before sampling. The maximum particle size was estimated by applying Stokes law for settling velocities. The maximum in the distribution of recorded ion bursts was estimated, and the corresponding number of ions calculated from the measured multiplier gain and analyzer transmission. The highest temperature point was obtained with Cr_2O_3 , the next highest with CuO , and lowest temperature, Pb_3O_4 .

A check of this method was made using $CsNO_3$ particles. Because of its extremely low ionization potential, Cs should be completely ionized. The particle diameters calculated for two different settling times were 1.3 and 0.7 μm , while the corresponding diameters calculated from the ion bursts were

1.1 and 0.6 μm , respectively. This shows that the method does not suffer from any gross errors.

From Figure 3, the various measurements produce a reasonably well-defined work function curve above about 1500 K, but the uncertainty progressively increases at lower temperatures. Various other observations, such as a broad maximum in the ion current vs. temperature curve for organic compounds at about 1100 K, indicated that the rhenium surface becomes fully covered at about this temperature and the work function then ceases to increase with decreasing temperature. The maximum value is probably 7.1-7.2 eV.

A third method that was tried used particles containing known ratios of two elements. One of the elements would be an easily ionized element like Li or Cs, while the other would have a high ionization potential. Measurements of the ratio of the output signals for the two elements would then allow one to calculate the ionization efficiency for the poorly ionized element. The particles were produced by preparing known concentrations of nitrates of the two elements in water and then using a fritted disc wetted by the solution to produce a fine mist of droplets. The droplets were then mixed with additional air to evaporate the water and form solid particles.

While this method should be quite accurate, the signal ratios obtained at 1190 K for Pb with Cs or Li varied by as much as a factor of 10. The higher values gave work functions around 7.1 eV, but the lower values approached 6.9 eV. The ratios obtained between two easily ionized elements (Li, Cs, U) were more consistent and reasonably close to the concentration ratios used. The reason for this variation was not determined. Possibly, the water vapor associated with this method affected the work function of the surface.

Also shown in Figure 3 are the results obtained by Greaves and Stickney for O_2 on polycrystalline Re (3). The disagreement between the two measurements may be caused by differences in the purity of the Re and hence differences in the recrystallization behavior when heated. Zehner and Farnsworth (4) found that at 1050 K, O_2 increased the work function of the 0001 face of Re by 1.7 eV but the 1010 face by only 1.5 eV. Fusy et al. (5), using recrystallized Re ribbon (preferentially oriented to the 0001 plane), obtained a maximum increase of 1.8 eV at 830 K. The work function change shown by the curve drawn in Figure 3 is 1.75, indicating that the ribbon used was also preferentially oriented to the 0001 face. The fraction of the surface covered by O_2 as determined by Weber et al. (6, 7) closely follows the same curve, indicating the work function change is approximately linear with oxygen

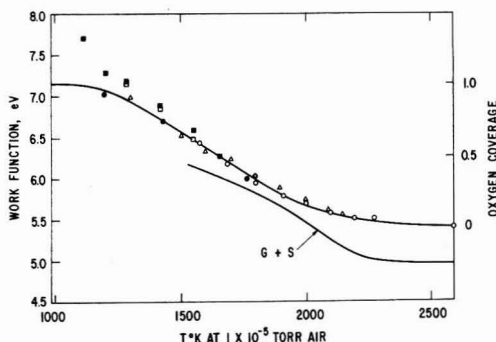


Figure 3. Measured values of work function of Re ribbon at approximately 10^{-5} torr air

Curve drawn is best estimate of true variation with temperature. Lower curve (G + S) is work function curve obtained by Greaves and Stickney (3). Work function: O, by electron emission; ■, from Pb^+ temperature variation; □, from Bi^+ temperature variation; ●, from ion yield based on Stokes law. Oxygen coverage: Δ, published data (6, 7)

coverage. The results of Fusy et al. (5) also show the same relationship.

Figure 4 shows the ionization efficiency $n_+/(n_0 + n_+)$ calculated from the Saha-Langmuir equation using $g_+/g_0 = 1$ and the work functions indicated by the curve of Figure 3. For high ionization potential elements, a maximum in the ionization efficiency occurs at 1100–1200 K in accord with experimental observations.

Particle Yield

The number of particles hitting the ionizing ribbon was observed to increase as the needle valve was opened to increase the flow rate, but at a pressure of about $3\text{--}4 \times 10^{-5}$ torr in the ionization chamber, a maximum was reached. At this point, the flow of atmospheric air at the inlet was about $24 \text{ cm}^3/\text{s}$. The particle yield was estimated by measuring the number of particles per cm^3 of air with a calibrated condensation nuclei counter and at the same time counting the number of particles hitting the ribbon and producing an ion burst at the detector. Room air contaminated with particles from a lighted match or tobacco smoke gave reasonably consistent results if the K^+ bursts were counted, but for best accuracy, synthetic aerosols of an alkali metal salt were used. The particulates in normal room air could not be depended on to always have sufficient K or Na in each particle to give reliable values for the particle yield. Often, only about $1/10$ the particles would be counted, possible because with the counting equipment used, the pulses from particles with small amounts of K or Na could be lost among the numerous large pulses.

The maximum particle yield measured was 0.3%, but 0.2% (one particle detected in 500 sampled) is a more typical value. This means that a particle density in the air of $20/\text{cm}^3$ will give 1 ion burst per second at the detector. The ion current background of the instrument normally consisted of a random emission of individual ions rather than bursts of ions so that detection of particle densities much less than 1 per cm^3 should be possible for many of the elements.

The most important parameters affecting the particle impingement rate appeared to be the pumping speed at the small intermediate chamber of the sampling system and the position of the end of the stainless steel tube with respect to the small sampling orifice. It is interesting to note that the ratio of the area of the orifice to the cross-sectional area of the inlet tubing is the same as the particle yield ($1/500$). In a separate experiment the spatial distribution of the particles at the filament plane was measured by impinging the particles on a greased plate. Most of the particles were found within a $1/2$ -mm diameter circle.

Ion Emission Rates

For most particles, the emission of metal ions showed an abrupt rise as the particle hit the ribbon followed by an approximately exponential decay with time. This is the behavior one would expect if the particle completely evaporated or diffused onto the surface of the ribbon in a time short compared to the residence time of the resulting atoms on the surface. Even at temperatures where the decay time was of the order of tens of microseconds, the rise to the maximum ion current was usually only about $10 \mu\text{s}$ (for example, CsNO_3 on W at 950°C). The most notable exception was exhibited by particles of CuO . For this compound the ion current would rise abruptly and decay slowly but would then abruptly drop to essentially zero long before completing the slow decay. This behavior suggests that the particle does not vaporize instantly but rests on the surface slowly feeding material to the surface until it is completely consumed. A more thorough study of the dynamics of ion emission would be needed, however, to determine exactly how the various kinds of particles interact with the hot surface.

The most complete study of the variation of the decay time constant with temperatures was made for Sr. This element (as well as the other alkaline earth elements) has a high affinity for W or Re surfaces, and the ions are emitted only at comparatively high temperatures. The rise time of the ion burst is very short compared to the exponential decay time. The latter were measured for SrCO_3 and SrCl_2 particles on W, and the results are plotted in Figure 5. As expected, the two compounds give identical results showing that the decay time is attributable to Sr rather than the compound. The points are not along a straight line probably because the oxygen coverage of the surface is changing with temperature. Müller and Wassmuth (8) found similar behavior and showed that the energy of desorption of Sr changed from 3.7 eV for clean W to about 5.2 eV for an oxygen-covered surface. Their values

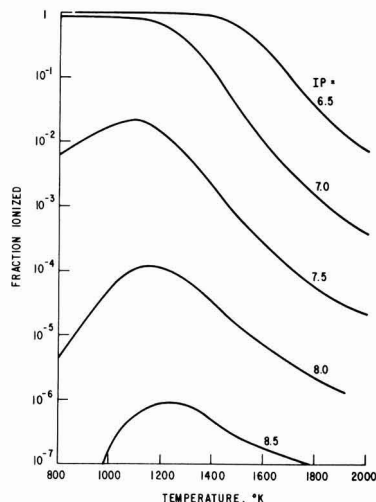


Figure 4. Calculated ionization efficiency for Re in 1×10^{-5} torr of air for range of ionization potentials (IP)

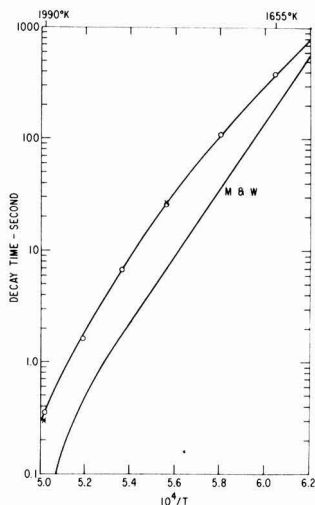


Figure 5. Time constant for exponential decay of Sr^+ from particles impinging on W
Lower curve derived from published data by use of molecular beams. O, SrCO_3 ; X, SrCl_2

for the decay time were measured as a function of work function change but by assuming published values of the work function of W in oxygen (3) are applicable to their tungsten sample, decay times corresponding to our conditions could be estimated (lower curve of Figure 5). If we consider our experimental errors and the assumptions involved in the calculation, the agreement can be considered satisfactory.

Results for Single Particles

The minimum amount of element in a particle that can be reliably detected is shown in Table I for some representative elements listed in order of increasing ionization potential. In all cases, the limitation is due to background ions arriving at the detector, not detector noise. The last column is the equivalent particle size calculated for the compound listed. Na, K, Rb, and Cs containing particles give results similar to Li with the minimum amount of element detectable being about 1000 atoms. The metal ions from particles of CaCO_3 , BaCO_3MoO , NiSO_4 , MgO , and BiCO_3 of less than $1 \mu\text{m}$ diameter were easily observed but GeO , WO_3 , Sb_2O_3 , CdO , and Zn were not detected, indicating the cutoff limit on ionization potential is about 8 eV. If ions of the element are emitted only at temperatures above the temperature corresponding to the maximum work function of O_2 covered Re, an even lower ionization potential would be necessary.

Figure 6 shows typical recordings of the ion bursts from natural particles in the air. These two recordings were taken within a few minutes of each other and show the relative particle densities for these two elements. The maximum bursts for K^+ correspond to about 5×10^5 atoms of K in the original particle, while those for Pb^+ correspond to about 2×10^6 atoms of Pb. The decay time of the pulses is due to the recorder, not the original signal.

Similar results for Li^+ are shown in Figure 7, but in this case, the sensitivity for the recording was increased to the point where background noise is observable. Many of the particle ion bursts overload both the electrometer and recorder, but a few very small bursts are also present. An ion burst of about 30 ions corresponding to 800 Li atoms in the particle is indicated, but most of the even smaller bursts are probably due to particles also.

Particle Size Distribution Measurements

If we assume the number of ions in the burst of ions produced as a particle hits the ribbon is proportional to the amount of element in that particle, pulse height analysis of the ion bursts should give a measure of the number of particles as a function of the amount of element per particle. If the particles have a constant known composition and density, one could also calculate the distribution in particle sizes from this data. No detailed study was made of this possibility, but a single measurement was made to indicate its feasibility.

The K^+ ion bursts from naturally occurring particles in the

laboratory air were counted as a function of the bias on the integral pulse height discriminator. The resulting integral pulse height distribution is shown in Figure 8. Also, shown are the particle concentration and the number of K atoms calculated from the measured data. The average number of K atoms per particle counted (total K atoms/total no. of particles) is approximately 2×10^5 . As the composition or density of the particles is not known, values for the particle size can only be estimated. Using a typical K concentration in air particulates of 1% and a particle density of 2 g/cm^3 yields a diameter of about $0.1 \mu\text{m}$ for a particle with 2×10^5 atoms of potassium. The mass median diameter (MMD) would be about $0.2 \mu\text{m}$ corresponding to 1.5×10^6 atoms of potassium. This MMD value is a reasonable one for indoor air (9).

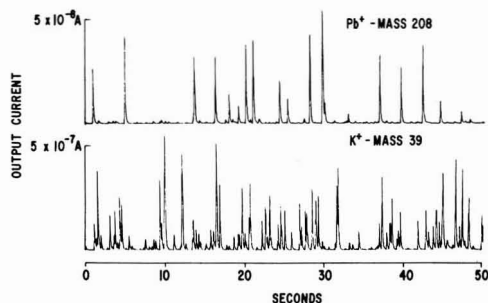


Figure 6. Typical output signals obtained for natural particles in laboratory air

Multiplier gain = 1×10^7 . Re temperature = 1200 K for Pb and 870 K for K

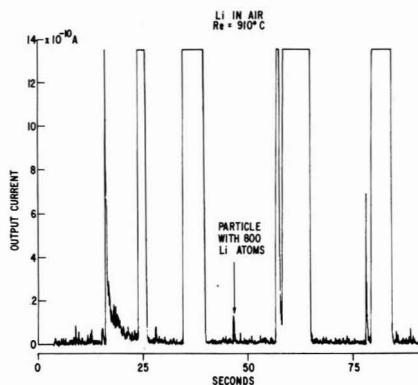


Figure 7. Bursts of Li^+ from natural particles

Multiplier gain = 6×10^6 ; Re temperature = 1180 K

Table I. Minimum Number of Atoms Detectable in Single Particles^a

Element	IP, eV	Re temp, °C	% Ions	10^3 Atoms	Compound	Particle diam, μm
Li	5.4	830	100	0.8	LiCO_3	0.004
Sr	5.7	1730	50	10	SrCO_3	0.01
U	6.1	1070	50	1.3	UO_2	0.006
Cr	6.8	1500	0.5	300	Cr_2O_3	0.02
Pb	7.4	910	3	200	Pb_3O_4	0.02
Cu	7.7	1130	0.02	7000	CuO	0.06

^a Particle size corresponding to this number of atoms was calculated for the compound listed.

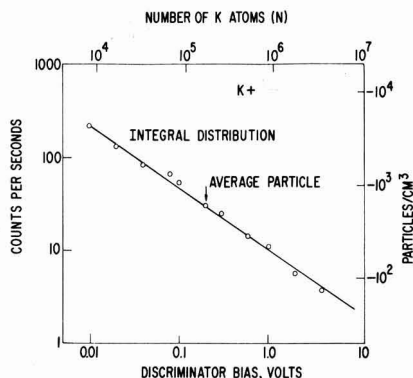


Figure 8. Integral pulse height distribution for K^+ ion bursts from laboratory air particles

Discussion of Results

The observed phenomena are in general accord with reported surface behavior, and the experimental measurements, both with known and natural particles, appear to be reasonable. The results are in general agreement with the independent study conducted by Myers and Fite (10). However, for this method of analysis to be put on a more firm foundation, some important questions must be answered.

One of the most important of these is the validity of the assumption that the number of ions in a burst is proportional to the amount of that element present in the particle. For example, the size and composition of the particle may have some effect on the ionization efficiency at the ribbon. If the atoms of the particle are spread over a large area of the metal surface by vaporization or diffusion before they evaporate as ions, one would not expect this effect to be large.

Another possible difficulty is that the transmission of the mass analyzer may depend to some extent on the area of the ribbon from which the ions are desorbed. Unless the particles are sufficiently collimated to hit only a small area or the atoms of the particle are spread over a large area of the surface before desorbing, some variations in transmission with impact position is to be expected. If the area of impact is indeed as small as the 0.5-mm diameter circle measured and the beam hits the center of the 3.2-mm wide ribbon, the variation in ion transmission should not be large.

Another source of error would be a variation in particle yield at the ribbon with the size and density of the particle. No attempt was made in the design of the sampling system to minimize particle size bias.

Some crude attempts were made to assess the importance of some of these possible errors, but the results were not conclusive. Probably the best way to measure these effects is to use a monodispersed aerosol generator to prepare and analyze particles of known size and composition.

Conclusions

This study has demonstrated the feasibility of continuous real-time analysis of airborne particulates by use of surface ionization mass spectrometry. Information can be obtained on the amount of a particular element present in each particle, the average amount per cm^3 of air, and the number of particles per cm^3 of air. For many elements the method is very sensitive, but unfortunately it is not a universal method. Unless a filament material with a higher work function than oxidized Re can be found, it is limited to elements with ionization potentials less than about 8 eV. Thus, many elements of interest such as Hg, Cd, Zn, As, or Be cannot be analyzed.

The accuracy of this method of analysis was not thoroughly investigated, but the results obtained so far indicate that at least semiquantitative measurements should be possible. Probably the most important next step in evaluating the applicability of this technique to atmospheric particle analysis is to determine for a variety of elements both the accuracy of the ionization efficiency predicted by the Saha-Langmuir equation and the constancy of this efficiency with particle size and composition.

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Continuous Mass Spectrometric Determination of Concentration of Particulate Impurities in Air by Use of Surface Ionization

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■ The average concentration of particulate impurities in air is determined by impinging the particles on a heated Re ribbon and analyzing the resulting ion current with a small magnetic sector mass spectrometer. Oxygen in the air raises the work function of Re to about 7.2 eV at 1000 K allowing analysis of elements with ionization potentials as high as 8 eV. In favorable cases, concentrations of 10^{-13} g/m³ can be detected. By collecting the particles on the ribbon for short periods and then flashing the filament, increased sensitivity can sometimes be achieved. Natural air particles are analyzed for Li, Na, K, Rb, Cs, Sr, U, Pb, Cr, and Cu. Large amounts of organic compounds are detected, but the mixture is too complex to positively identify individual components.

An instrument for the analysis of single particles by use of surface ionization was described previously (1). By directing a high velocity stream of air against an orifice, an aerosol beam is formed which is directed against a heated Re ribbon in a mass spectrometer ion source. As each individual particle hits the ribbon, a burst of ions is produced which is then focused and analyzed. The number of ions in the burst is a measure of the number of atoms of that element in the particle.

If analysis of single particles is not necessary, one can lower the temperature of the ribbon until the desired degree of signal integration is obtained and measure the average ion current produced. The concentration in the air can then be estimated from the particle efficiency (fraction of particles sampled that hit the ribbon and are analyzed), the analyzer transmission (fraction of ions produced at the ribbon which arrive at the detector), and the ionization efficiency for the particular element. An advantage of this technique is that the lower operating temperature produces a higher work function surface and hence increases the ionization efficiency for elements with a high ionization potential. In some cases, there is the additional advantage that the background level is reduced. This article describes the results obtained by use of this technique.

Results

An example of the results obtained for Li in ambient laboratory air is shown in Figure 1 and for Pb in Figure 2. Before the start of each recording, a filter to remove particulates is inserted in the sampling line to show the background signal of the instrument. A summary of some representative results obtained by this method is shown in Table I. The concentrations listed were calculated with a particle efficiency of 0.2% and an analyzer transmission of 4%. The ionization efficiency was estimated from the Saha-Langmuir equation and the measured work function of the Re (1). The air flow was 24 cm³/s.

The background levels for high mass elements such as Pb and U were caused primarily by organic compounds in the vacuum system and hence could be improved by using more care to obtain a clean system. The backgrounds for Na and K were caused primarily by the elements themselves present in the filament material. At the low temperature used, the alkali metal was not diffusing to the surface of the Re in appreciable quantities, but instead volatile Re oxides were being formed which exposed the alkali metal. For example, the K⁺ back-

ground under vacuum or with N₂ applied to the sample inlet was less than 1 ion per second but with air applied to the inlet, the background immediately rose to about 20 ions/s. The Ca, Ba, Sr, and Cr backgrounds appeared to be caused primarily by evaporation of compounds of these elements from nearby surfaces. The surfaces were undoubtedly contaminated by the large amounts of pure compounds of these elements used during the preliminary phases of this study, and the backgrounds are probably not representative of a clean ion source. Similarly, the high Cs background is due to the use of CsNO₃ during bakeout to activate the electron multiplier.

In addition to the instrumental backgrounds listed, interference can also be produced by the particles themselves. Besides the obvious case of interferences from ions of the same mass (organic ions being the most troublesome here), there exists the possibility of ions of different mass being scattered or reflected into the mass position being measured. For natural particles the most troublesome offenders are Na⁺ and K⁺. The degree to which this broad background of scattered ions interferes with the analysis depends on the proximity of the mass desired to the masses of K⁺ and Na⁺. For the rather modest mass analyzer used in this study, the Na⁺ and K⁺ ion current was attenuated by a factor greater than 10⁶ outside the mass range 20–50.

The ambient levels in laboratory air shown in the last column were taken at random intervals of time and do not necessarily represent comparative concentrations of elements for any one time. As an example of a comparative analysis, the concentrations of Li, Na, K, and Pb were measured over a short interval of time as 6, 30, 50, and 700 ng/m³, respectively. The condensation nuclei counter indicated 17 000 particles/cm³ at this time.

Analysis by Particle Collection Technique

For some elements, lower concentrations can be measured by turning off or reducing the current to the ionizing ribbon, collecting particles on the cooler surface for about a minute or longer, and then rapidly reheating the ribbon to obtain a burst of metal ions. This technique is especially applicable to

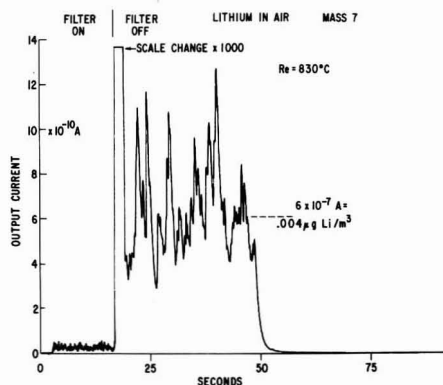


Figure 1. Measurement of average concentration of Li in laboratory air
Multiplier gain = 6×10^6

those elements like Pb or U where the background is caused primarily by organic compounds. About 1 or 2 orders of magnitude gain in signal-to-noise level can be obtained, probably because interfering organic compounds are too volatile to be absorbed.

The results obtained for Pb by completely turning off the heating current are shown in Figure 3. A small burst of ions (presumably organic) is obtained even for the filter on, but even so the background burst is a factor of 1200 less than the Pb⁺ burst, indicating an equivalent instrument background level of about 0.06 ng Pb/m³, about a factor 10 improvement over constant temperature operations.

Better results are usually obtained by lowering the temperature of the ribbon to some intermediate temperature which is sufficiently cool to retain the metal atoms but hot enough to oxidize or prevent condensation of the organic compounds. Figure 4 for U shows that by using 600 °C as the lower temperature, the organic interference can be essentially completely eliminated. The organic ions continue to evolve at the lower temperature. From this figure, one can estimate that the instrumental background is roughly equivalent to 0.0003 ng U/m³. The burst of UO₂⁺ is roughly proportional to collection time.

This mode of operation should also be helpful with other types of background problems where the interfering element or compound is more volatile than the desired element (for example, if scattered K⁺ ions are interfering with the measurement of Ca⁺ at mass 40). The increase in signal level alone that can be achieved with collection techniques is potentially useful, but at the present stage of instrument development, detector noise is not a significant problem.

Environmental Measurements

Because the equipment was not designed to be portable, measurements of environmental samples were confined to laboratory air. The building is well ventilated, however, and when analysis of the outside air was desired, the windows were opened. The following observations are given to indicate the potential usefulness of this method of analysis.

Lead. Except for the alkali metals, lead was the most prominent metal impurity observed in spite of the fact that its ionization efficiency is only about 3% and the laboratory is located in a semirural area. The Pb concentration was typically about 0.1 μg/m³, while the average urban concentration in the U.S. has been stated as about 0.8 μg/m³ (2). It was interesting to note, however, that the concentration

Table I. Concentrations of Several Elements in Laboratory Air

Element	IP, eV	Re temp, °C	% Ionized	Background level, ^a ng/m ³	Lab air, ng/m ³
Cs	3.9	600	100	0.002	2
Rb	4.2	600	100	0.0008	0.05
K	4.3	600	100	0.0004	0.5–200
Na	5.1	600	100	0.0004	0.4–40
Li	5.4	840	100	0.0001	0.1–6
Sr	5.7	1500	100	0.02	10
U	6.1	1070	50	0.003	<0.003–0.7
Cr	6.8	1130	50	0.005	0.05
Pb	7.4	910	3	0.6	60–600
Cu	7.7	1000	0.1	1	<1–15

^a Background levels refer to filtered air.

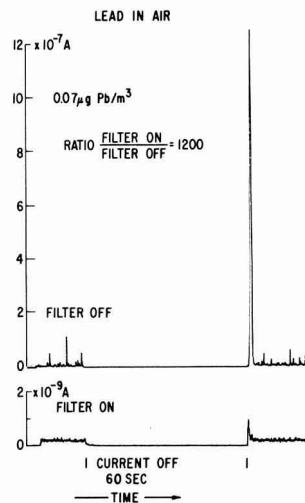


Figure 3. Burst of Pb⁺ produced by heating ribbon to 920 °C after collecting natural air particles on cold ribbon for 1 min. Bottom record shows background of interfering ions when particles are excluded by filter.

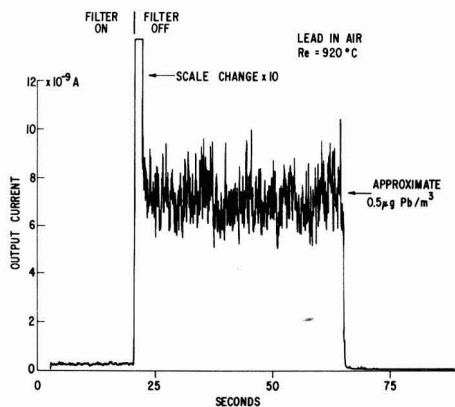


Figure 2. Measurements of average concentration of Pb in laboratory air. Multiplier gain = 6 × 10⁶

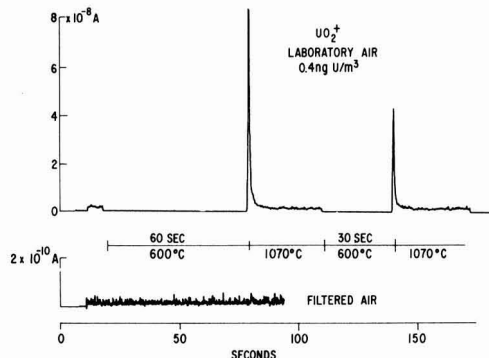


Figure 4. Burst of UO₂⁺ produced by heating ribbon to 1070 °C after collecting natural air particles on ribbon at 600 °C for both 1- and ½-min periods. Bottom record shows absence of burst of ions if particles are filtered out.

markedly increased when laboratory employees started their automobiles at the end of the working day even though the instrument is about 50 ft above the parking lot. Figure 5 shows this effect for the two groups of employees quitting work at 4:30 and 5:00 p.m. This effect was observed even if the windows were closed. The maximum peak ever observed was about $2.5 \mu\text{g}/\text{m}^3$. The minimum Pb level of about $0.02 \mu\text{g}/\text{m}^3$ was observed after a cold front had passed through this location and the strong wind was from the NW (polar air from Canada).

Uranium. The uranium level in the air was usually not readily observable ($<0.003 \text{ ng}/\text{cm}^3$). Uranium in the spectrum became obvious only during a strong long-lasting inversion on the East Coast during the summer months. A prominent peak at mass 270 (UO_2^+ -uranium was the only element that was observed to emit a compound ion) indicated a U concentration of $0.7 \text{ ng}/\text{m}^3$ at this time. The average pulse height corresponded to about 1300 U atoms/particle. The concentration gradually declined over several days until it was again difficult to detect among the organic peaks. Conventional mass spectrometric analysis of a sample taken at a nearby suburban location (Scotia) 3 years earlier showed a value of $0.03 \text{ ng}/\text{m}^3$ and at an urban location (Albany), $0.5 \text{ ng}/\text{m}^3$ (3).

Chromium. While Cr does not have a particularly large ionization potential, it desorbs from Re with difficulty, and at the high temperatures required for rapid desorption (1500°C), the surrounding parts of the ion source gradually become sufficiently heated to evaporate considerable amounts of Cr and cause a high background signal. A likely source of this Cr is the stainless steel parts used to construct the ion source. By operating at low temperatures, the background levels of Table I could be achieved at the expense of a response rate of several minutes.

Figure 6 is a mass scan of the Cr isotope region showing the Cr level in the air at this time to be about $0.05 \text{ ng}/\text{cm}^3$. A check of the isotope abundances at masses 50, 53, and 54 gave good agreement with the known values. The average urban concentration has been reported as $15 \text{ ng}/\text{m}^3$ (2), a much larger value than reported here. Operation of an ordinary 500-W nichrome heater in the room gradually increased the Cr level to $0.4 \text{ ng}/\text{m}^3$ as shown in the third scan from the bottom. The peaks at mass 55–60 have not been identified but are largely organic in nature.

Copper. Copper is near the limit of the ionization potentials that can presently be ionized effectively. Ordinarily, it was not detectable in normal room air ($<1 \text{ ng}/\text{m}^3$), but a single value of $15 \text{ ng}/\text{m}^3$ was observed. The average urban concentration has been reported to be $90 \text{ ng}/\text{m}^3$ (2).

Figure 6 shows the result of operating a small electric drill in the room. The arcing and wear at the copper commutator were sufficient to produce a copper concentration of $60 \text{ ng}/\text{m}^3$. Mass 63 and 65 can be seen to have approximately the correct ratio of 2.2 for the two copper isotopes.

Lithium. The observed Li isotope ratio was the natural ratio within the experimental error. On a typical day the particle concentration obtained by counting ion bursts was 2100 particles per cm^3 . The condensation nuclei counter indicated a total of 20 000 particles/ cm^3 ; therefore, only about 1 particle in 10 contained enough Li to give a count (>1000 atoms of Li). The average ion burst corresponded to about 1.3×10^5 Li atoms per particle which yields a Li concentration of $3 \text{ ng}/\text{m}^3$. The concentration obtained by measuring the average ion current was approximately this value, indicating that most of the Li was concentrated in 10% of the particles in the air.

Strontium. Strontium is easily ionized, but prolonged operation of the ion source at the high temperatures required to evaporate this element causes the background of Sr^+ to

greatly increase. Until this occurred, however, Sr in the air was easily detectable. The measured concentration of $10 \text{ ng}/\text{m}^3$ agrees with the average value reported for a statewide survey of Texas (4).

Organic Compounds. Many organic compounds are efficiently ionized on oxidized Re. Nicotine, for example, yields about 2 A of ion current at the Re ribbon per torr of nicotine or an ionization efficiency of 20%. The spectrum produced is similar to but less complicated than that from electron bombardment and is shown in Figure 7. It is because of this high

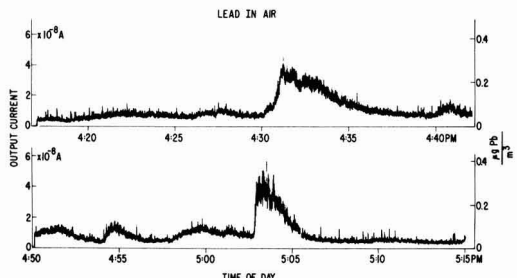


Figure 5. Continuous recording of Pb^+ signal during late afternoon showing increase in Pb concentration caused by automobiles

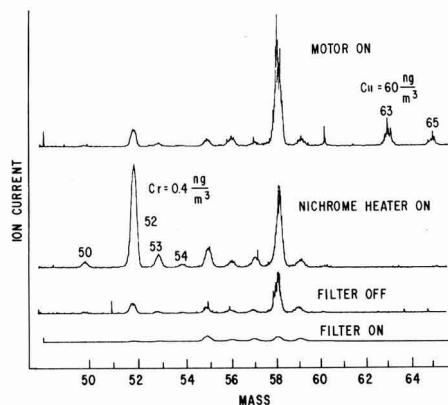


Figure 6. Output signal as analyzer scans mass 50–65 region showing Cr and Cu in laboratory air
Lowest curve shows background spectra in absence of particles

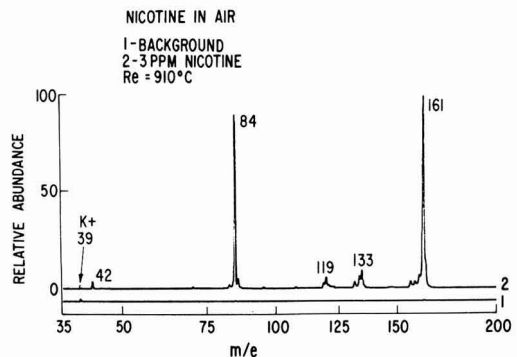


Figure 7. Mass spectrum produced by 3 ppm nicotine (mass 162) added to air
Lower curve indicates background from filtered normal air

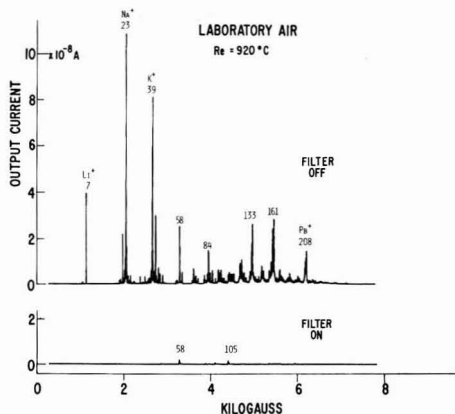


Figure 8. Complete mass spectrum produced by particulates in laboratory air

Abscissa is field of magnetic analyzer. Two prominent peaks (mass 58 and 105) in lower background spectrum are due to organic compounds in vacuum system

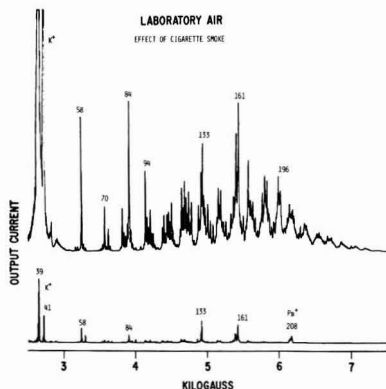


Figure 9. Mass spectrum produced by lighted cigarette in room (upper) compared to spectrum of normal laboratory air (lower)

efficiency that organic vapors in the vacuum system are so troublesome. A pressure of only 2×10^{-14} torr of nicotine in the vacuum system would yield the same ion current as about 1 ng/m^3 of Cs in the air.

Figure 8 shows a complete mass scan for normal laboratory air. The temperature of the Re is that which gives the maximum ion current for most organic compounds. The clearly identifiable inorganic peaks are due to Li^+ , Na^+ , K^+ , and Pb^+ with mass 133 being partially due to Cs^+ . The remainder of the ion peaks are caused largely by organic compounds in particulate form or adsorbed on inorganic particulates. Unfortunately, the limited resolution of the mass spectrometer, the large number of peaks, and the lack of reference spectra do not allow an unambiguous interpretation of this spectrum. However, the same mass peaks, 84 and 161, that are prominent in the nicotine spectrum are also prominent in the room air spectrum, suggesting that the building air is contaminated with tobacco smoke and that the nicotine concentration in the air is about 2 ppb. A lighted cigarette placed in the room gives about the same spectrum (Figure 9) but at about an order of magnitude higher intensity. The nicotine concentration in the air of 20 ppb indicated by this result agrees with the value estimated from the average nicotine content of cigarettes and the air flow and volume of the room.

If we assume no interference from other organic compounds, the minimum concentration of nicotine in air that is detectable in this analyzer is about 0.01 ppb. In a separate mass spectrometer system using a mercury diffusion pump, the organic background was reduced sufficiently to allow detection of this and other efficiently ionized organic compounds at about the 0.001 ppb level. A more complete report on the surface ionization of organic compounds will be published separately.

For analysis of inorganic elements in particular, it would be desirable to eliminate the organic compounds present. One possible method of doing this is to heat the incoming air stream sufficiently hot to burn up the organic matter. When a quartz tube was attached to the inlet of the sampling system and heated to 600–800 °C, the organic peaks did indeed largely disappear without appreciably affecting the known inorganic peaks such as the alkali metals and Pb. This technique was not thoroughly explored, however, and the optimum conditions were not established.

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Chemiluminescence Measurement of Reactivity Weighted Ethylene-Equivalent Hydrocarbons

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■ A reactive hydrocarbon analyzer (RHA), based on the chemiluminescent reaction of hydrocarbons with oxygen atoms, is used to provide a rapid indication of reactivity weighted hydrocarbon mass in automobile exhaust. Samples are reported by their ethylene-equivalent concentration—the concentration of ethylene which would give the same mass-reactivity product as the exhaust hydrocarbon mixture. These are compared to ethylene-equivalent concentrations obtained by the much more cumbersome procedure of weighting the individual sample hydrocarbons, determined by gas chromatography (GC), by their respective relative short-term photochemical reactivities, summing these results, and equating them to ethylene. Procedures are also described to eliminate a negative interference to the RHA method resultant from H₂O quenching of the chemiluminescence emitter. The RHA and GC ethylene-equivalent concentrations correlate within 5%.

Hydrocarbon emissions from motor vehicles are controlled primarily because of their role as precursors of oxidant compounds formed in the atmospheric photochemical system (1). The reaction rates of the hydrocarbons in the atmosphere are variable (2–6). That is, some classes of hydrocarbons react very rapidly in the photochemical system, contributing significantly to oxidant levels near the hydrocarbon sources, while other classes of hydrocarbons react slowly, contributing more significantly to oxidant levels downwind of the sources.

Methods are available for detailed determination of auto exhaust hydrocarbon composition by gas chromatography (7). If the concentration of each hydrocarbon is determined, a reactivity index for the sample can be developed by weighting each hydrocarbon by its specific reactivity. Many reactivity scales have been proposed. In 1974 Dimitriadis reviewed existing laboratory evidence and developed a reactivity classification scheme based on the oxidant-forming potential of organics under urban atmospheric conditions (6). The hydrocarbons were weighted by their short-term reactivities. The Dimitriadis scheme categorizes organic emissions into five classes in which the automobile exhaust hydrocarbons fit as follows:

Reactivity class	Relative molar reactivity rating	Auto exhaust hydrocarbons
I (nonreactive)	1.0	C ₁ –C ₃ paraffins, acetylene, benzene
II (reactive)	3.5	Mono- <i>tert</i> -alkyl benzenes
III (reactive)	6.5	C ₆ ⁺ paraffins, cycloparaffins, alkyl acetylenes
IV (reactive)	9.7	<i>Pri</i> - & <i>sec</i> -mono and dialkyl benzenes
V (reactive)	14.3	Aliphatic olefins tri- & tetra-alkyl benzenes

The numerical ratings are based on the average photochemical reactivity of the respective class of organics normalized to the nonreactive Class I organics.

An auto exhaust analytical method is available by which the hydrocarbon components in each of these groups are mea-

sured directly and collectively (8). The method utilizes gas chromatography for determination of Class I hydrocarbons and subtractive techniques for Classes III–V. Although this method is a more practical approach than detailed analysis of each hydrocarbon by gas chromatography, it is still very time consuming and costly to perform.

In recent years there has been considerable effort in the study of gas-phase chemiluminescence reactions of hydrocarbons (9–11). These studies indicated that possibly an analytical procedure could be developed which would measure hydrocarbons in a manner correlating with their photochemical reactivity. That is, hydrocarbons with high photochemical reactivity would give a more intense instrumental response per unit concentration than hydrocarbons with low photochemical reactivity.

In 1974 Baity et al. reported a gas-phase chemiluminescence procedure for detection of hydrocarbons based on reaction with atomic nitrogen (12). The procedure corresponded reasonably well to reactivity weighted mass except for a disproportionately high response to acetylene. The method was also troubled by high sensitivity to sample oxygen level. Fontijn and Ellison recently developed a gas-phase chemiluminescence method for measurement of reactive hydrocarbons based on reaction with atomic oxygen (13). This approach is attractive because the analyzer gives a “real-time” response to sample hydrocarbons which is proportional to both mass and photochemical reactivity. Of course, the procedure does not measure photochemical reactivity directly since the chemistry of the method is significantly different from that of the atmosphere. But it does respond to hydrocarbons in a manner which can be made to correlate with reactivity weighted mass.

This paper will describe the application of that system to motor vehicle exhaust samples. The analyzer reacts the sample hydrocarbons with O-atoms at reduced pressure. The difference between the OH ($A^2\Sigma - X^2\Pi$) emission intensities at 308.9 and 312.2 nm is measured and found to be proportional to both the mass and photochemical reactivity of sample hydrocarbons. For acetylene $I_{308.9} \approx I_{312.2}$; hence, no measurable signal is generated, while for ethylene $I_{308.9} \gg I_{312.2}$. Methane yields no observable emission. The other hydrocarbons have spectral distributions similar to ethylene.

Experimental

The flow scheme of the chemiluminescence reactive hydrocarbon analyzer (RHA) is shown in Figure 1.

In conjunction with previously established procedures, the microwave power is maintained at 20%. A reagent gas of 10% oxygen in argon is used in the discharge as a source of O-atoms. The chemiluminescence reactor is maintained at 1.6 torr, 0.8 torr sample and 0.8 torr reagent gas. To calibrate the instrument, it is “zeroed” with a hydrocarbon free zero grade air and with a sample of acetylene 100 parts-per-million molar (ppmM) in air. The acetylene sample is used to equate the 308.9- and 312.2-nm channels to produce zero response in the differential amplifier. The instrument is then spanned with

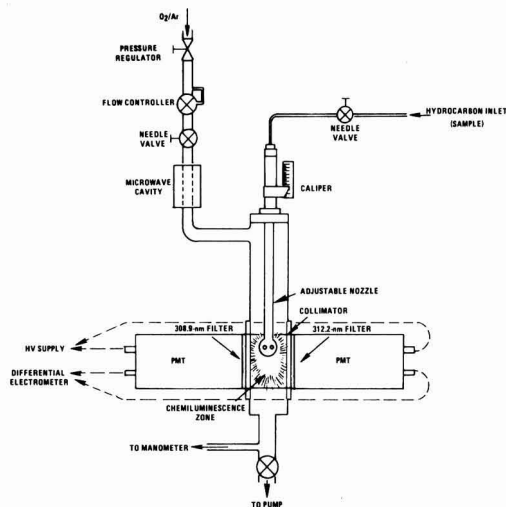


Figure 1. Flow scheme of chemiluminescent hydrocarbon analyzer

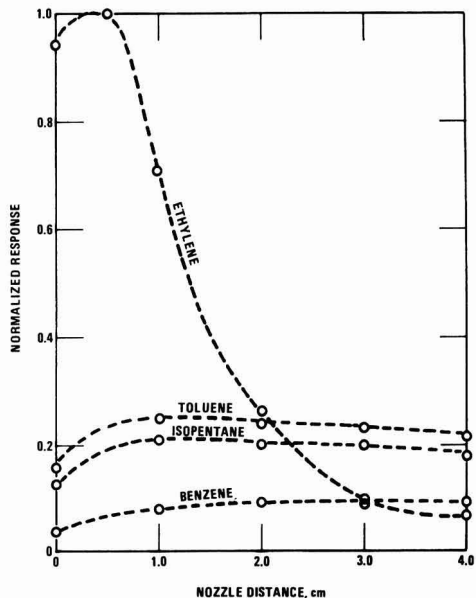


Figure 2. Hydrocarbon response as function of analyzer nozzle placement (Hydrocarbons are of equivalent molar concentration)

Table I. Rate Constants for Reaction of Atomic Oxygen (O^3P) with Organic Compounds in Gas Phase^a

Compound	Rate constant $\times 10^{-7} \text{ Lmol}^{-1} \text{ s}^{-1}$	Temp, K
Ethylene	49	298
Toluene	14	298
Isopentane	8	307
Benzene	2.4	298

^a As recommended by Herron and Huie (14).

ethylene in air, and results are reported as ethylene-equivalent hydrocarbon.

To permit empirical validation of the results obtained with RHA, procedures have been established to calculate the ethylene-equivalent concentration of samples based on detailed gas chromatographic hydrocarbon data. The ethylene-equivalent concentration is obtained by determining the molar concentration of each hydrocarbon in the sample; weighting these values according to their respective reactivities (from the Dimitriadis scale); summing and dividing by 14.3, the molar reactivity index assigned to ethylene:

Ethylene-equivalent concentration, ppmM

$$= \frac{\sum_{\text{HC}} (\text{Concn, ppmM} \times \text{HC reactivity index})}{14.3} \quad (1)$$

Methane and acetylene, compounds of very low photochemical reactivity, are excluded from the calculation since the response of the instrument to these compounds is zero by design. The ethylene-equivalent concentration then would represent the ethylene concentration capable of causing the same short-term urban oxidant as the auto exhaust sample.

A key parameter in the determination of the relative response of the RHA to specific hydrocarbons is nozzle spacing—the distance of the nozzle tip to the center of the observation zone. As shown in Figure 1, the sample hydrocarbons are mixed with O-atoms at the nozzle tip. Figure 2 illustrates the relative intensities of the chemiluminescence of equivalent molar concentrations of four specific hydrocarbons as a function of nozzle distance. The relative intensities at short nozzle distances are ordered by the relative reaction rates of the hydrocarbon with O-atoms. The O-atom reaction rates are given in Table I. Compounds of high reaction rate, such as ethylene, demonstrate rapidly decreasing intensity with in-

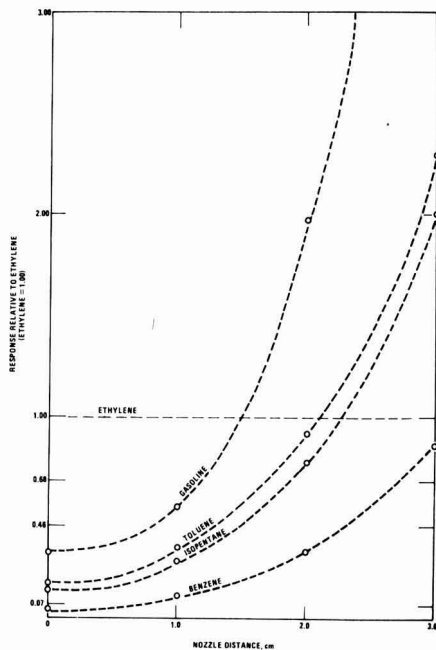


Figure 3. Analyzer response to hydrocarbons relative to ethylene as function of nozzle placement

Table II. Gas Chromatographic Analysis of Hydrocarbon Samples

Compound	Gasoline in air		1972 Chev exhaust		1974 Mazda exhaust	
	A ^a	B ^b	A _c	B _c	A _c	B _c
Methane						
Ethylene			9.58	136.04	13.76	196.70
Ethane			0.77	0.76	1.34	1.34
Acetylene						
Propylene, propane			2.94	42.04	3.64	52.00
Propadiene			0.26	3.37	0.26	3.67
Methyl acetylene			0.36	2.34		
Isobutane	0.065	0.424	0.19	1.25	0.43	2.81
Butene-1, isobutylene			0.90	12.80	0.86	12.26
<i>n</i> -Butane, 1,3-butadiene	1.314	10.643	1.00	8.08	2.10	16.99
<i>trans</i> -2-Butene	0.047	0.669	0.12	1.75	0.18	2.54
<i>cis</i> -2-Butene			0.06	0.89	0.08	1.11
3-Methyl-1-butene			0.01	0.20	0.03	0.49
Isopentane	1.700	11.050	0.83	5.42	1.61	10.47
Pentene-1	0.013	0.186	0.02	0.31	0.05	0.69
<i>n</i> -Pentane, 2-methyl-1-butene	0.247	9.105	0.60	4.38	1.05	7.68
<i>trans</i> -2-Pentene	0.054	0.772	0.04	0.63	0.05	0.77
<i>cis</i> -2-Pentene	0.077	1.098	0.07	1.00	0.03	0.43
2-Methyl-2-butene	0.706	10.096	0.37	5.26	0.50	7.18
Cyclopentane, 3-methyl-1-pentene	2.462	16.006	0.88	5.73	1.68	10.89
2,3-Dimethylbutane	0.108	0.701	0.06	0.38	0.07	0.44
2-Methylpentane, 2,3-dimeth-1-butene	0.141	0.985	0.09	0.62	0.09	0.60
3-Methylpentane	0.063	0.406	0.05	0.31	0.04	0.24
1-Hexene, 2-ethyl-1-butene	0.027	0.379	0.02	0.29	0.03	0.45
<i>n</i> -Hexane, <i>cis</i> -3-hexene	0.051	0.329	0.05	0.33	0.03	0.18
2-Methyl-2-pentene	0.072	1.032	0.03	0.45	0.03	0.43
Methylcyclopentane, 3-meth- <i>trans</i> -2-pentene	0.083	0.579	0.05	0.37	0.03	0.23
2,4-Dimethylpentane	0.047	0.303	0.03	0.20	0.03	0.17
Methylcyclopentene	0.025	0.353				
Benzene, cyclohexane	0.051	0.194	1.65	6.28	1.51	5.73
Cyclohexene, 2,3-dimethylpentane, 2-methylhexane	0.875	6.213	0.25	1.79	0.42	3.00
3-Methylhexane	0.139	0.905	0.07	0.45	0.07	0.48
Isooctane	1.470	9.552	0.37	2.39	0.64	4.17
<i>n</i> -Heptane	0.210	1.365	0.06	0.41	0.08	0.55
Methylcyclohexane	0.113	0.736	0.03	0.20	0.05	0.33
2,4 and 2,5-Dimethylhexane	0.252	1.635	0.07	0.44	0.11	0.72
2,3,4-Trimethylpentane	0.153	0.995				
2,3,3-Trimethylpentane	0.068	0.440	0.06	0.36	0.80	0.49
Toluene, 2,3-dimethylhexane	2.916	27.991	2.45	23.56	2.78	26.67
2-Methylheptane	0.288	1.869	0.10	0.64	0.17	1.11
3-Methylheptane	0.260	1.690	0.08	0.52	0.13	0.85
2,2,5-Trimethylhexane	0.040	0.260	0.03	0.17	0.02	0.14
<i>n</i> -Octane	0.183	1.189	0.08	0.50	0.09	0.56
2,3,5-Trimethylhexane	0.005	0.035	0.002	0.01	0.00	0.02
2,4-Dimethylheptane	0.023	0.150	0.01	0.05	0.01	0.07
2,5- and 3,5-Dimethylheptane	0.043	0.281	0.01	0.07	0.02	0.14
Ethylbenzene, 2,3-dimethylheptane	0.128	1.201	0.13	1.18	0.22	2.10
<i>p</i> -Xylene, <i>m</i> -xylene, 4-methyloctane	0.651	6.121	0.48	4.48	0.13	1.23
<i>o</i> -Xylene, unk C ₉ paraffin	0.207	1.982	0.23	2.21	0.22	2.12
Nonane	0.057	0.371	0.02	0.11	0.03	0.20
<i>n</i> -Propylbenzene	0.031	0.301	0.01	0.12	0.02	0.18
1-Methyl 3-ethyl-benzene, unk C ₁₀ paraffin	0.125	1.192				
1-Methyl-2-ethylbenzene, unk C ₁₀ paraffin			0.07	0.65	0.12	1.12
Mesitylene	0.085	0.823	0.06	0.60	0.05	0.51
1,2,4-Trimethylbenzene	0.128	1.238	0.10	0.97	0.07	0.67
<i>Sec</i> -butylbenzene, <i>n</i> -decane	0.020	0.156	0.01	0.08	0.02	0.19
Unknowns	0.999	8.095	0.42	3.39	0.52	4.19
Total	17.82	142.1	26.23	286.83	35.58	388.3

^a A: concentration, parts-per-million molar. ^b B: reactivity index (concentration X molar reactivity rating). ^c Methane and acetylene are excluded due to their zero response in the RHA.

creased nozzle spacing due to the rapid depletion of the organic.

Ideally, the nozzle distance would be selected to best approximate the relative responses dictated by the reactivity scale selected as the base for the sample indexing procedure. Figure 3 shows the response of various hydrocarbons relative to ethylene as a function of nozzle distance. As suggested by the Dimitriades reactivity scale, the instrumental response to the nonreactive Class I hydrocarbons should average about 7% of the ethylene response, (1.0/14.3)100. Similarly, the C₄⁺ paraffin response about 45.4% of the ethylene response, and the aromatics less benzene about 67.8% of the ethylene response.

Selection of a nozzle distance appropriate for auto exhaust based on the response of single compounds would be a very cumbersome task because of the large number of hydrocarbons found in exhaust samples. Therefore, an empirical determination based on a known mixture of gasoline was used. Gasoline is a good choice since nearly all hydrocarbons C₄ and above, which are found in auto exhaust, are found in gasoline. The only hydrocarbon of significance to the method in exhaust, less than C₄, is propylene. Methane and acetylene are abundant, but give zero response in the RHA. Ethylene is also abundant, but it is the calibration compound and the procedure normalizes all hydrocarbons to ethylene.

Table II gives the detailed chromatographic analysis of the gasoline sample and the quantities used to predict the ethylene-equivalent concentration. Applying Equation 1:

$$\text{Ethylene-equivalent concentration} = \frac{142.1}{14.3} = 9.9 \text{ ppmM}$$

The actual molar concentration of the sample was 17.8 ppmM, indicating that the desired instrument response to gasoline relative to ethylene should be 0.56. By placing the nozzle at 1.0 cm, an ethylene-equivalent response of 9.8 ppmM could be obtained.

An auto exhaust sample, obtained from a 1972 Chevrolet, was then analyzed with the nozzle set at 1.0 cm. The detailed results are presented in Table II. The chromatographically predicted response was 20.1 ppmM ethylene equivalent. The actual response of the RHA, however, was 17.6 ppmM, 88% of the theoretical value. In the original work (13) it was determined that 3% water vapor caused a 12% reduction in ethylene response, probably due to a "quenching-effect" with the radiating specie. Auto exhaust samples contain water vapor, potentially to saturation, at room temperature. The samples are collected with air dilution in "Tedlar" bags, and the actual water vapor level is determined by the dilution ratio and the relative humidity of the dilution air.

Quenching effects were investigated for a number of hydrocarbons which are known to be abundant in auto exhaust. The response to specific hydrocarbons in dry air was compared to the response in air saturated with water. The "wet" samples contained 3.3 ± 0.2% water vapor. The water levels were measured optically with a prototype infrared analyzer (15). The response to the wet samples was corrected for dilution by the added water vapor. Determinations were made at both 1.0- and 1.6-cm nozzle distances. The results are given in Table III. The average ratio of wet to dry response was 0.86 ± 0.07 at 1.0 cm and 0.88 ± 0.03 at 1.6 cm. These results suggest that the erroneously low results obtained for auto exhaust at a 1.0-cm nozzle distance were due to water quenching.

Procedures were then investigated to alleviate the negative interference of water vapor. Figure 3 suggests that by increasing the nozzle distance, a net gain in the response to the hydrocarbons relative to ethylene could be obtained. This gain could be selected to offset the negative interference of the water vapor. The exhaust sample from the 1972 Chevrolet previously discussed (Table II), when analyzed with the RHA

Table III. H₂O Quenching Effect Expressed as Ratio of Wet Response to Dry Response

Compound	Nozzle distance, cm	
	1.0	1.6
Ethylene	0.88	0.85
Propylene	0.94	0.89
Toluene	0.88	0.72
Isopentane	0.88	0.85
Benzene	0.72	0.88
Cyclohexane	0.84	0.88
<i>n</i> -Pentane	0.83	0.89
<i>p</i> -Xylene	0.86	0.88
Butene-1	0.98	0.90
<i>n</i> -Butane	0.82	0.87
Isooctane	0.82	0.89
2-Methyl-2-butene	0.84	0.83

nozzle set at 1.55 cm, gave 20.0 ppmM ethylene-equivalent. This value compares very favorably with the chromatographically predicted 20.1 ppmM.

Three other exhaust samples were analyzed with the nozzle set at 1.55 cm, and the results are listed in Table IV. The ratio of RHA to theoretical values varied from 0.97 to 1.25. This procedure is appropriate if the sample water concentrations are relatively constant, but it is not sensitive to changes in water concentration. If the dilution air is dry, the sample water level will be low, and the corresponding negative interference will be lessened. Thus, the results will be erroneously high. A more attractive approach to the problem would be to remove the water prior to analysis, hopefully with little change to the sample hydrocarbons.

A commercial device appearing to offer potential is the Perma Pure dryer, which uses the principle of selective permeation across a membrane material. The membrane is formed in a tube bundle through which the sample is pumped. The water permeates the walls of the tubes and is pumped away, while the hydrocarbons pass through the tubes unchanged.

To verify the selective removal of water, a gasoline sample was saturated with H₂O and analyzed before and after the dryer by gas chromatography. The water level was lowered from 3.3 to 0.1%, and the hydrocarbons were quantitatively transmitted through the dryer. The wet sample had 60.2 ppmM total hydrocarbon (THC). If no hydrocarbons were lost in the drying process, about 62.0 ppmM THC would be expected due to the effective concentration of the sample resultant from removal of the water. Actually observed was 60.1 ppmM THC, indicating a net loss of 1.9 ppmM or about 3.1%.

Several samples were then analyzed with the Perma Pure dryer for water removal. The RHA analyzer nozzle was set at 1.0 cm. Table IV presents the data from these analyses. The exhaust values were about 5% low. This deviation is due, in part, to the loss of hydrocarbons during the drying process, and in part, to the varying character of exhaust versus gasoline hydrocarbons. In addition to the presence of the low-molecular-weight hydrocarbons in the exhaust, the relative abundances of the higher-molecular-weight hydrocarbons are different from gasoline. This is particularly true for olefins where the test gasoline level was 7.4 wt % and exhaust levels two to three times that value are common (16).

The loss of hydrocarbons in the drying process can be compensated for by nozzle adjustment as discussed earlier. A final exhaust sample was run with the dryer and with the RHA nozzle set at 1.2 cm. This sample was from a 1974 Mazda

Table IV. Samples Analyzed with RHA

Sample	Nozzle distance, cm	Perma Pure dryer used	RHA ethylene-equiv concn, ppmM	Theoret ethylene-equiv concn, ppmM	Ratio, RHA/theoret
1972 Chev exhaust	1.00	No	17.6	20.1	0.88
1972 Chev exhaust	1.55	No	20.0	20.1	1.00
1976 Maverick exhaust	1.55	No	11.0	11.3	0.97
Chrysler "lean-burn" prototype A exhaust	1.55	No	12.0	10.0	1.20
Chrysler "lean-burn" prototype B exhaust	1.55	No	11.0	8.8	1.25
Gasoline in air, dry	1.00	Yes	33.3	33.6	0.99
Gasoline in air, 3.3% H ₂ O	1.00	Yes	31.5	33.6	0.95
Gasoline in air, 3.3% H ₂ O	1.00	No	28.5	33.6	0.85
AMC Hornet prototype exhaust	1.00	Yes	4.8	5.0	0.96
1974 Mazda exhaust	1.00	Yes	36.6	38.4	0.95
1974 Mazda exhaust	1.20	Yes	27.0	27.2	0.99

and is detailed in Table II. The theoretical ethylene-equivalent concentration was 27.2 ppmM; the RHA value was 27 ppmM.

Conclusions

Hydrocarbons vary in their potential for participation in atmospheric photochemical reactions leading to oxidant formation. Some are more "reactive" than others and contribute more significantly to urban air pollution. A gas-phase chemiluminescence procedure based on the reaction of hydrocarbons with O-atoms is a viable analytical procedure for predicting the "ethylene-equivalent concentration" of auto exhaust samples. The only other analytical procedure permitting this correlation involves very complex, time consuming, and expensive gas chromatographic methods.

The chemiluminescence analyzer response correlates well with the reactivity weighted mass of the compounds being analyzed. The prototype analyzer as described by Fontijn et al. (17) has a noise limited detection of 0.05 ppmM ethylene-equivalent hydrocarbon. The long-term stability of the analyzer is excellent with zero and span drift less than 0.10 ppmM/h after the instrument has equilibrated. The precision of the system is greater than ±2% of the mean. The accuracy is dependent on initial instrument setup with the nozzle distance being very critical. As illustrated in Figure 3, the response of gasoline relative to ethylene varies dramatically with nozzle distance. With the nozzle distance properly selected and sample water levels reduced with the Perma Pure dryer, agreement within 5% of theoretical can readily be achieved.

In routine application of the instrument to complex hydrocarbon samples, a calibration mixture of character similar to the sample should be used to establish the nozzle placement. For example, a blend of the test gasoline could be used for auto exhaust studies. The nozzle distance can be selected to obtain whatever response relative to ethylene the selected reactivity scheme suggests.

The technique is very simple to apply. It offers real-time response to hydrocarbon samples proportional to their reactivity weighted mass.

Acknowledgment

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Wastewater Treatment by Liquid Membrane Process

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■ A liquid membrane process is being developed for application to a number of industrial waste treatment problems. The results of laboratory and pilot plant studies show that liquid membranes are capable of reducing the levels of NH_4^+ , Cr^{6+} , Cu^{2+} , Hg^{2+} , and Cd^{2+} from several hundred ppm to less than 1 ppm under batch or continuous flow conditions.

Wastewater treatment is a problem of major proportions throughout the industrialized world (1-5). Recently, Japan has experienced a pressing need for new safe, economical methods for processing wastewater containing such toxic heavy metal ions as Cr^{6+} , Hg^{2+} , Cd^{2+} , and Cu^{2+} as well as nitrogenous compounds such as NH_4^+ which cause supernutritive conditions in river and seawater. This paper discusses the application of liquid membrane technology to solving some of these problems. The results of both laboratory experiments and pilot plant runs for removal of NH_4^+ , Cr^{6+} , Hg^{2+} , Cd^{2+} , and Cu^{2+} are described.

Liquid membranes were invented by Li in 1968 (6, 7) and have been proposed as solutions to a number of waste disposal problems (5, 8-12). They are water-immiscible emulsions consisting of an oil phase composed of surfactants and various additives in a hydrocarbon solvent which encapsulates microscopic droplets of an aqueous solution of appropriate reagents for removing (stripping) and trapping wastewater contaminants. A conceptualized drawing of a liquid membrane "capsule" is given in Figure 1. The example shown is for removal of ammonia from wastewater such as that from a sewage plant. In the effluent from such a plant, ammonia exists in mobile equilibrium with the ammonium ion:



At a pH > 9 the unionized form greatly predominates. The molecular form of ammonia (NH_3) has appreciable oil solubility and readily permeates from the outside aqueous phase through the oil membrane into the encapsulated aqueous acid where it is trapped in the form of the oil insoluble ion (NH_4^+). The example shown depends upon the pollutant (NH_3) having an appreciable oil solubility. This is not a requirement since additives can be incorporated in the membranes to enhance solubility and permeation rates. For example, heavy metal ions that cannot normally permeate oil membranes can be removed from aqueous solutions by incorporating a suitable ion transport facilitator (ion carrier) in the oil phase. The mechanism of facilitated transport through liquid membranes has been discussed by Li et al. (9, 10).

Experimental

General Procedure for Preparation of Liquid Membrane Emulsions. A solution of the trapping agent (internal phase) in water (total of 50 g) was added dropwise to a stirred solution of surfactant and additives in oil (total of 100 g) contained in a baffled, 2-L resin kettle. The resulting emulsion was stirred at 1000-2000 rpm for 10-20 min at ambient temperatures to ensure complete encapsulation. The oil phase of the emulsion used for ammonia removal was similar to the one discussed previously (8, 11-14). A typical formulation was

0.1% span 80 (sorbitan monooleate), 3% of a nonionic polyamine described previously (8, 11) which acts as a membrane strengthening additive, and 86% of an isoparaffinic solvent which is made by Exxon. This solvent has an average molecular weight of 386.5, a cloud point of 93 °F, a pour point of 90 °F, and a specific gravity of 0.85 at 78 °F. For separations of inorganic ions, an ion carrier was added to the oil phase. This was Alamine 336, a C_8 - C_{10} tertiary amine for chromium and mercury removal (15, 16), Lix 64N, a mixture of two oxime compounds for copper separation (17), or Aliquat 336 (methyltriocetyl ammonium chloride) for cadmium removal (18). All ion carriers were obtained from the General Mills Corp.

Laboratory Test Procedure. The appropriate liquid membrane emulsion (50 g) was added to a 2-L baffled resin kettle containing the wastewater feed solution to be extracted (100-500 g). The two-phase system was stirred by means of a variable speed mixer equipped with two marine-type propellers with three blades each. Mixing speed ranged from 200 to 400 rpm. The uptake of the pollutant was monitored by removing samples of the feed solution periodically for analysis. Atomic absorption techniques were used for Cd^{2+} , Cr^{6+} , Cu^{2+} , and Hg^{2+} , while NH_4^+ was determined by means of an ion electrode.

Experiments with Two-Stage Counter-Flow Pilot Equipment. The flow diagram for the two-stage continuous counter-flow pilot plant is shown in Figure 2. This equipment has a maximum treating capacity of 30 L/min of wastewater and is adaptable to batch, semibatch, or continuous (occurrent and countercurrent) conditions by exchanging the piping trains. Wastewater is sent into mixing column No. 1 by a dosing pump and mixed with the liquid membrane emulsion. While the mixture of wastewater and emulsion passes up through the mixing column, the heavy metal or other toxic substance is concentrated in the emulsion. The overflow from the mixing column is led to the settler No. 1, and then wastewater and emulsion are separated by gravity. The wastewater which leaves the settler No. 1 is sent into the mixing column No. 2 and treated in a second stage extraction. Fresh emulsion is pumped from the fresh emulsion tank to mixing column No. 2 for the second stage extraction. Since the circulating emulsion from the second stage extraction is only partly saturated, it is recycled back to the first stage by means of the emulsion

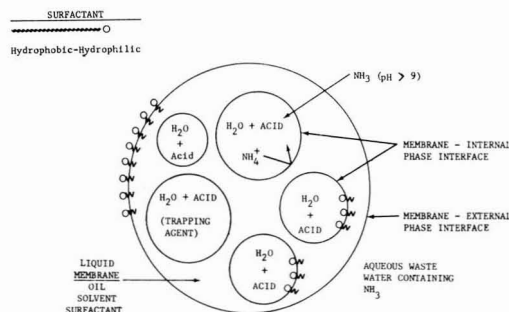


Figure 1. Schematic diagram of liquid membrane capsule

transfer pump. The spent emulsion from the first stage is drawn off for reconditioning or disposal.

A detail of the mixing column is given in Figure 3. The column consists of three Pyrex cylinders of 7.6 and 15.2 cm each, separated by glass plates with a 20-mm centered opening. Two flat-blade turbines are set in each compartment, and four verticle baffles are provided to afford optimum mixing conditions.

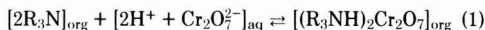
Results and Discussion

Removal of NH_4^+ in Laboratory Batch Experiments.

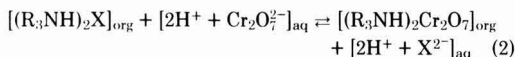
The NH_4^+ ion is removed in the form of NH_3 as described in the example given above (Figure 1). In laboratory experiments using wastewater from a sewage plant, the NH_4^+ concentration was reduced from about 50 to 0.37 ppm after 20 min treatment (Figure 4). The three curves were obtained with three liquid membranes differing in viscosity. They show that the separation rate increased with decreasing viscosity of the membrane phase, even though the treat ratios were in the opposite direction, varying from 1/3.1 to 1/5.2 in curves 1-3. Higher treat ratios normally result in slower extraction rates.

Removal of Heavy Metal Ions by Laboratory Batch Experiments. The transport of metal ions across the liquid membrane barrier is an excellent example of "facilitated transport" (10). This is exemplified by the chemistry of chromium transport (15):

Extraction by amine neutralization

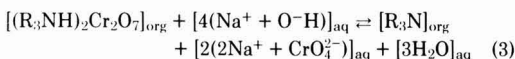


Extraction by salt formation

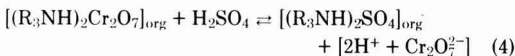


The extraction of $\text{Cr}_2\text{O}_7^{2-}$ by either Equation 1 or 2 occurs at the membrane-external phase interface (Figure 1). The exact extraction mechanism depends upon the stripping agent employed, Equation 3 or 4. Stripping of the metal ion, which occurs at the membrane-internal phase interface, is accomplished by one of two methods (15):

Basic stripping



Acid stripping



Stripping with a base regenerates the free amine in the membrane which then reextracts additional $\text{Cr}_2\text{O}_7^{2-}$ by Equation 1. Acid stripping regenerates the amine salt for extraction as shown in Equation 2. Both methods have been used successfully in liquid membranes. One of the important advantages of the liquid membrane process lies in the concurrent extraction and stripping in a single stage rather than two separate stages as required by solvent extraction. In addition, by concurrently extracting and stripping, the liquid membrane process drives the equilibrium of extraction as shown in Equations 1 and 2 to the right by removal of the complexed ions as formed. This removes a serious limitation inherent in some solvent extraction methods.

Some of the typical results of laboratory experiments are given in Figure 5 and Table I. Figure 5 (Curve 1) shows that in a batch run nearly complete chromium removal was achieved in 10 min with a feed containing an initial chromium concentration of 400 ppm. The results of experiments at two

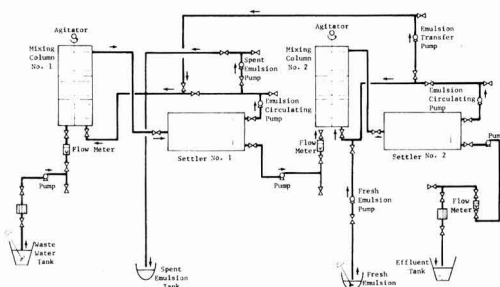


Figure 2. Two-stage continuous countercurrent pilot plant

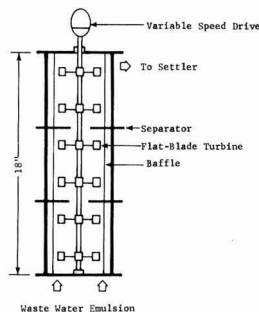


Figure 3. Detail of mixing column

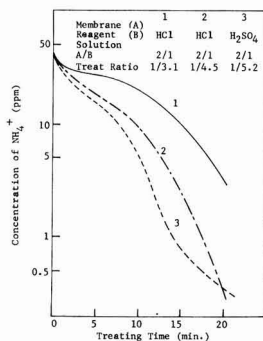


Figure 4. Removal of NH_4^+ from sewage in laboratory batch experiments

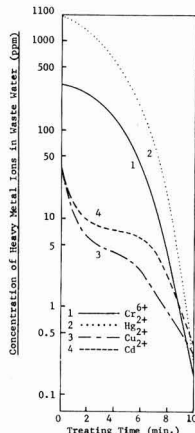


Figure 5. Removal of heavy metals in laboratory batch experiments

different external pH values are given in Table I. These data indicate that in order to transfer chromium from the external feed to the internal reagent phase of the liquid membrane emulsion, the pH of these two phases must be controlled to within certain critical limits. At a constant basic pH of the internal phase, given by the 2% NaOH aqueous solution, the transfer of chromium was very fast when the external phase was acidic. The Cr^{6+} content of the external phase was reduced from 390 to 12 ppm (97% removal) in 15 min under these conditions. However, under basic conditions, no transfer of chromium was observed.

Figure 5 also shows the removal of mercury, copper, and cadmium (curves 2–4, respectively), by the facilitated transport mechanism in liquid membrane systems. Solvent extractions of these metals have been reported (16–18). The reported techniques employ two-step procedures (extraction plus stripping) similar to those shown above for chromium. The liquid membrane system combines the extraction and stripping into one step.

Table I. Effect of External pH on Chromium Removal from Wastewater by Liquid Membrane Emulsions^a

pH of external phase		Contact time, min					
		0	5	10	15	20	30
3.5	ppm Cr^{6+}	390	250	80	12	3	2
7.0	ppm Cr^{6+}	390	(No removal)				390

^a Conditions: reagent phase = 2% NaOH; feed = 0.1% $\text{K}_2\text{Cr}_2\text{O}_7$; membrane/reagent wt ratio = 1.2; feed/emulsion = 3.1; temperature = 25 °C.

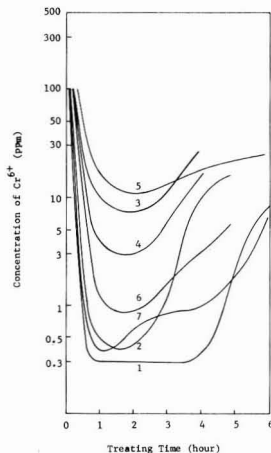


Figure 6. Removal of Cr^{6+} in single-stage pilot plant experiments. Curve numbers correspond to test runs shown in Table III

Table II. Test Conditions for Pilot Plant Run (Figure 6)

	Test run						
	1	2	3	4	5	6	7
	Internal reagent, 10% NaOH						
Reagent (l)/membrane (M)	1/2	1/2	1/2	1/2	1/2	1/2	1/2
Agitation, rpm	300	200	300	300	300	300	300
Feed flow rate (VF), cc/min	150	150	340	250	150	150	150
Treat ratio ^a	1/5	1/5	1/10	1/7	1/5	1/5	1/5

^a Treat ratio = weight emulsion/weight wastewater feed.

Although the general principle is the same, the removal of Cd^{2+} represents a somewhat different problem. In the effluent from metal plating baths, cadmium exists as the tightly bound cyanide complex:



This complex is readily extracted from aqueous solutions by liquid ion-exchange agents such as Aliquat 336 (methyltriethylammonium chloride) (18). However, stripping is quite difficult because of the great stability of the $\text{Cd}(\text{CN})_4^{2-}$ complex under basic conditions ($K_{ST} = 10^{19}$) (19). The usual stripping agents, salts and mineral acids, are ineffective even at high concentrations. Ethylenediaminetetraacetic acid (EDTA) is known to chelate strongly with cadmium complexes (20). In the form of its disodium salt, EDTA successfully removed cadmium from Aliquat 336 with regeneration of the ion carrier so long as the pH of the internal phase of the emulsion was maintained in the range of 4–6. The results shown in Figure 5 (curve 4) were obtained using the Aliquat-EDTA system.

Test Results with Pilot Plant Equipment—Single Stage. Preliminary experiments with a single-stage pilot plant were performed prior to studying the two-stage continuous operation. This was done to determine the characteristics of the equipment and establish the lifetime of the emulsion. Wastewater containing 100 ppm of Cr^{6+} from a plating process was continuously supplied during this test.

Figure 6 shows a plot of treating time vs. concentration of Cr^{6+} in the outside (feed) phase. The conditions employed are shown in Table II. The most favorable results were obtained when the test conditions of 10% NaOH reagent solution, a ratio of reagent solution to membrane of 1/2, and 300-rpm mixing speed were adopted (run No. 1). Note that the concentration of Cr^{6+} is plotted on a log scale in Figure 6. The best run gave a chromium removal from 100 to 0.3 ppm (nearly 100% removal). The emulsion was capable of maintaining this low level for up to 4 h without regeneration. Even after 5 h the Cr^{6+} in the feed was reduced to under 1 ppm. This represents a 99% removal. Thus, 45 L of wastewater were purified continuously to a Cr^{6+} level of 1 ppm by 920 g of the liquid membrane emulsion in about 5 h. The Cr^{6+} content of the spent emulsion was about 65 500 ppm. The consumption of the internal reagent amounted to 50%.

Experiment with Two-Stage Continuous Equipments. Based on the test results of the single-stage experiments and in cases when the wastewater and liquid membrane emulsion were supplied in a countercurrent flow as shown in Figure 2, the operational conditions by which stable and continuous treatment could be achieved were studied. The test conditions and results are given in Table III. In all cases, the concentration of Cr^{6+} in the effluent water was continuously and stably reduced from 100 to below 1 ppm. Final consumption rates of emulsion and concentration of Cr^{6+} in the emulsion were 25% and 35 800 ppm in test No. 1, 33.2% and 108 000 ppm in test No. 2, and 56% and 182 000 ppm in test No. 3, respectively.

Table III. Removal of Cr⁶⁺ by 2-Stage Pilot Plant

Feed to test unit; wastewater containing 100 ppm Cr⁶⁺ from plating process

Test no.	Test no.		
	1	2	3
LM emulsion			
Membrane (A)			
Reagent solution (B)	10% NaOH	20% NaOH	20% NaOH
B/A	1/2	1/2	1/2
Flow rates, cc/min			
Wastewater	300	300	300
Emulsion	280	105	064
Treat ratio	1/4.85	1/4.85	1/3.40
Mixing speed, rpm	200	200	300
Concn of Cr ⁶⁺			
After treatment			
In effluent	1 ppm	1 ppm	1 ppm
In emulsion	35 800 ppm	108 000 ppm	182 000 ppm

At present, there is no good process that can efficiently and economically remove heavy metals and ammonia from wastewater. Therefore, a considerable incentive exists to develop a process to fill such a need. Pilot plant tests and economic analyses on the liquid membrane process are continuing to achieve final commercialization. Emphasis in these tests is on regeneration of the membrane and recovery of valuable metals. The results obtained thus far on the removal of cad-

mium, mercury, copper, and ammonia from various wastewater streams have been quite encouraging.

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Photooxidation of *n*-Hexadecane Sensitized by Xanthone

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■ The photosensitized oxidation of hexadecane on water is studied as a model system for the solar dissipation of oil spills. Xanthone acts as a sensitizer forming hexadecanol with a quantum yield, at 313-335 nm, of 0.60-0.16 depending on intensity. Yields of peroxides are about 1% of the alcohol produced. A mechanism is proposed consistent with the alkylperoxy radical detected by ESR.

The possibility and probability of oil spills in remote inaccessible regions must be anticipated. Normal methods (1) are ineffective for areas such as the Arctic, and it is with this aspect in view that this work was undertaken. It is believed that the addition (from an aircraft, for example) of a suitable sensitizer to an oil spill should accelerate the solar photosensitized oxidation and solubilization of the oil.

Recently, it has been shown (2-6) that certain compounds can be used as sensitizers to accelerate the photochemical oxidation of hydrocarbons. The primary requirements of a suitable sensitizer are: stability in the oil-water system, strong absorption in the visible or near UV region, a triplet state of sufficiently high energy so that a free radical chain reaction

capable of proceeding at low temperatures may be initiated, lipophilic and hydrophobic properties, and stability under conditions which prevail during the oxidation of the oil. We have studied the following compounds as sensitizers: chloranil, anthraquinone (62), carbazole (70), xanthone (74), 1-naphthol (58), triphenylamine (70), 2'-acetonaphthone (59), 1-cyanonaphthalene (57), and thioxanthone (65) (the energies in kcal/mol of the corresponding triplet state are indicated in parentheses). Based on results of GLC analysis of the oil layer and on the UV spectra of the aqueous layer of the irradiated samples as compared to control samples (not irradiated) of *n*-hexadecane saturated with sensitizers, xanthone was found to be most effective and thus was selected as the sensitizer in the study of this model system.

In the photochemical oxidation of hydrocarbons (7), the products are generally alcohols, ketones, aldehydes, acids, peroxides, and hydroperoxides. Klein and Pilpel have shown (2-5) that alcohols were the major product from *n*-hexadecane and that peroxides and hydroperoxides accounted for about 10% of the products.

We have also examined the photosensitized reaction using ESR. Based on the product analyses, quantum yields, and the ESR results, a mechanism (Type I) is proposed for the oxidation in which xanthone (triplet) abstracts a hydrogen atom from the hydrocarbon to initiate a free radical chain reaction.

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Experimental

The hydrocarbon used was *n*-hexadecane, 99% pure from Aldrich Chemical Co. It was further purified by oxidizing the impurities with concentrated sulfuric acid with a small amount of potassium permanganate and chromatographing the hydrocarbon twice through an activated silica gel column. The purified hexadecane was then checked for impurities by GLC and UV absorption spectroscopy. All water used was freed of organic contaminants (distilled from alkaline permanganate and acidic dichromate) as evidenced by far UV absorption spectrum. Xanthone from Aldrich was used without further purification. The saturated sample solutions of sensitizer in *n*-hexadecane contained about 10 mmol/L of xanthone. The alcohol standards were prepared from hexadecanols obtained from Sample Chemical Co. with minimum purities of 99%.

A Westinghouse 400-W mercury lamp (#H33-1-CD) with a Nonex glass envelope and an Hanovia S500 lamp (8) were used as UV sources. Various filter combinations were used to isolate different wavelengths for irradiation. Radiation intensities were determined with the potassium ferrioxalate actinometer (9). Quantum yields at 313–335 nm were made using the filter combination (10) of Corning #7-54 and NiSO₄ in a Pyrex cell.

A solution of *n*-hexadecane saturated with sensitizer (1 mL) was added to the cell (4 cm diameter) containing 40 mL of water (organic phase about 1 mm in thickness). During the photolysis, air was passed through the cell above the oil film at a flow rate of 20 mL/min while the temperature was maintained at $24^\circ \pm 1^\circ\text{C}$ with a continuous flow of water through the cell jacket. Aliquots of oil film were obtained at various time intervals with a 10- μL Hamilton syringe. The increasing alcohol concentration in the sample was monitored by GLC. The gas chromatograph (equipped with flame ionization detector) was a Hewlett-Packard Model 402 fitted with a 6-ft copper column ($\frac{1}{8}$ in. o.d.) packed with chromosorb W (80–100 mesh AW-DMCS) coated with 10% OV-17 at 175 $^\circ\text{C}$. The concentration of xanthone in the *n*-hexadecane was also determined periodically by GLC at 190 $^\circ\text{C}$. The trace C₁₇ component in hexadecane (corrected for partial reaction by the yield of alcohol) was used as the internal standard since the exact volume of the sample, which often contained water, was not known. Separation of the various isomeric hexadecanols was not complete, and total integration of the peaks was used to indicate total alcohol. Alcohol concentration in the oil after 96 h of photolysis was also determined by acetylation (2). The agreement between the two methods was within 2%. Peroxides and hydroperoxides were determined iodometrically (11).

The cavity of a Varian E-3 ESR spectrometer was rotated through 90 $^\circ$ to allow the insertion of a quartz tube (11 mm o.d.) horizontally in the cavity. This tube contained a quartz boat with a raised platform to allow only a thin water film in the center of the cavity (Figure 1). The hydrocarbon film containing the sensitizer was floated onto the water layer in the boat and irradiated in the cavity from above. A continuous flow of air (saturated with water) was maintained during the photolysis. The UV light source (8) was used in conjunction with a Vycor filter. The buildup of free radicals during irradiation, their decay in the dark, and their dependence on oxygen were determined for hexadecane solutions of xanthone and 1-naphthol. The *g*-values of the radicals were determined relative to DPPH. Chromatograms of the alcohols in the irradiated boat were similar to the products obtained during the irradiation in the cell.

Results and Discussion

The yields of total alcohols as a function of irradiation time are shown in Figure 2 for xanthone in *n*-hexadecane. The

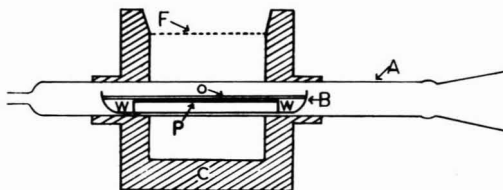


Figure 1. Quartz boat in ESR cavity (schematic diagram—not to scale)

A: 11-mm o.d. quartz tube. B: Quartz boat with raised platform P. C: ESR cavity. W: Water. O: Oil film with sensitizer. F: Cavity window for UV beam

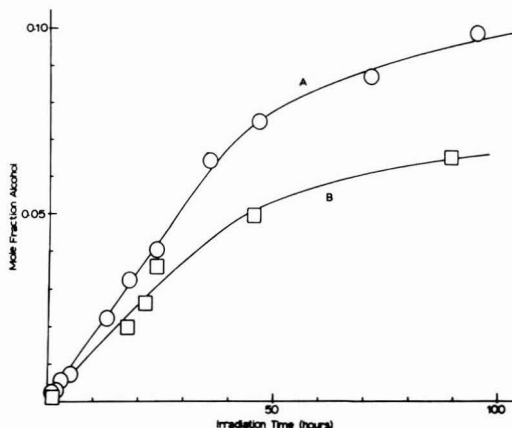


Figure 2. Yield of hexadecanol as function of irradiation time
Curve A: Vycor filter, xanthone ~ 10 mM. Curve B: 313–335 nm, xanthone 6.37 mM. Absorbed intensity $\sim 1.2 \times 10^{-7}$ Einstein/min

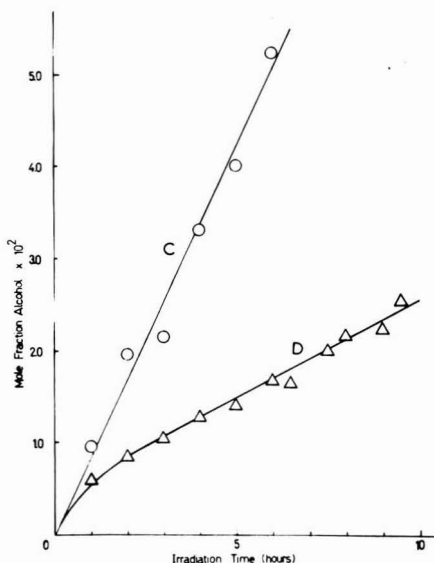


Figure 3. Yield of hexadecanol as function of irradiation time
Curve C: Bright sunlight, xanthone 4.43 mM. Absorbed intensity $\sim 6 \times 10^{-7}$ Einstein/min. Curve D: 313–335 nm, xanthone ~ 3.77 mM. Absorbed intensity $\sim 7.25 \times 10^{-7}$ Einstein/min

initial rate of formation of the alcohol at 313–335 nm is 7.3×10^{-8} mol/min. The intensity of the lamp at this wavelength region as determined by actinometry was 1.2×10^{-7} Einstein/min. The absorption at these wavelengths by xanthone (6.37×10^{-3} M) is complete (OD = 4) and gives a quantum yield for alcohol formation of about 0.60. At higher intensities of incident radiation, corresponding more closely to the solar flux, the rate of formation of alcohol is much higher. This is shown in Figure 3 for unfiltered bright sunlight (Curve C) and for filtered UV (313–335 nm) at 7.25×10^{-7} Einstein/min (Curve D) where the quantum yield for alcohol formation was calculated to be about 0.16.

The effect of irradiation time on the xanthone concentration is shown in Figure 4. After irradiation for a period of 25 h (Curve A, Figure 2 and Curve X, Figure 4), the extent of decomposition of xanthone is about $1.5 \mu\text{mol}$ which corresponds to the formation of about $200 \mu\text{mol}$ of alcohol. At higher intensities (Curve D, Figure 3 and Curve Y, Figure 4) the corresponding values after 5 h of irradiation are $1.5 \mu\text{mol}$ of xanthone decomposed and $52 \mu\text{mol}$ of alcohol formed. This shorter chain length at higher intensities is probably due to radical-radical reactions which would also account for the lower quantum yield for alcohol formation. This implies that a long free radical chain reaction is producing the alcohol and/or that the xanthone is being regenerated after initiating the reaction.

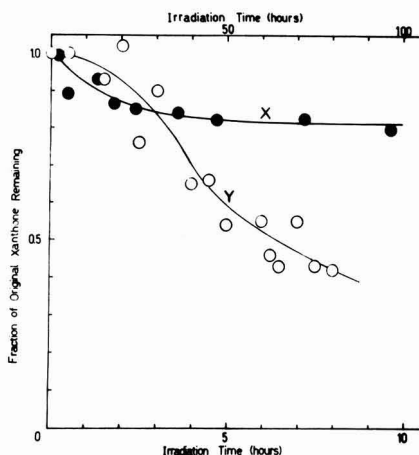


Figure 4. Proportion of xanthone undecomposed as function of irradiation time

Curve X: (Upper abscissa—filled circles) Conditions as in curve A, Figure 2. Curve Y: (Lower abscissa—open circles) 313–335 nm, xanthone 4.43 mM. Absorbed intensity $\sim 7.25 \times 10^{-7}$ Einstein/min

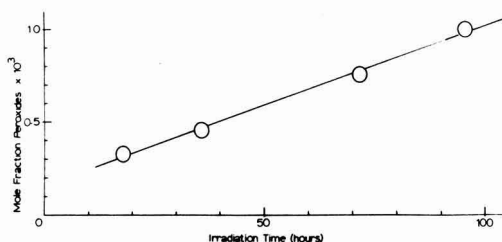


Figure 5. Yield of peroxide as function of irradiation time (condition as in Curve A, Figure 2)

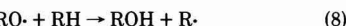
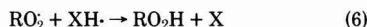
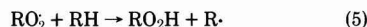
The falloff in rate of formation of alcohol at low intensities (Figure 2) may be due to the formation of di- and trihydroxy hydrocarbons, though this explanation is inconsistent with the agreement between the results obtained in the two methods for alcohol analysis.

Figure 5 shows the yields of peroxides and hydroperoxides as a function of irradiation time. The ratio of peroxide/alcohol from xanthone is about $1/10$ that obtained by Pilpel from 1-naphthol and implies a different reaction mechanism is operative especially in view of the greater susceptibility of the 1-naphthol to oxidative destruction compared to xanthone. This was verified by the ESR spectra obtained from the two systems. The photolysis of xanthone in a *n*-hexadecane film on water in the presence of air gives a single line ($g = 2.015$, line width 9G) which decays in the dark in a few seconds. The radical could not be detected in the absence of oxygen. This radical is believed to be the alkylperoxy radical (RO_2) (12, 13).

A different single line spectrum was obtained in the 1-naphthol system ($g = 2.002$, line width 10G). This radical, which has not as yet been identified, decays slowly in the dark ($t_{1/2} \approx 1$ h) and was also observed when nitrogen, instead of air, was passed over the boat.

When both sensitizers were present in the hydrocarbon film, the free radical due to 1-naphthol appears first followed, after prolonged irradiation, by the RO_2 radical. In the dark the RO_2 radical disappears in seconds, whereas the radical 1-naphthol decays slowly.

The Type I photosensitized oxidation mechanism (14) can best account for the results, viz.,



where X = xanthone, X^* = xanthone triplet, and RH = *n*-hexadecane. Reaction 1 represents the formation of triplet xanthone via the excited singlet. The activation energy for Reaction 2 is small [approximately 3 kcal/mol for benzophenone (15)]. Reactions 3 and 6 result in the regeneration of the sensitizer. The remaining reactions are well known and have been studied extensively (7, 12, 13).

Radical-radical interaction (other than Reaction 6) leading to chain termination and the decomposition of the xanthone also occur. When xanthone was added to a crude oil film on water, the RO_2 radical was not observed, probably due to the high absorption of the oil at the sensitizing wavelength. However, a noticeably different chromatograph was obtained for a GC analysis of the irradiated oil sample as compared to the control.

The effect of temperature at constant irradiation intensity was studied for the xanthone photosensitized oxidation of *n*-decane since this hydrocarbon is liquid at 0 °C. The results showed that under identical irradiation intensities and xanthone concentration, within experimental error (about $\pm 5\%$), there was no difference in the rates of formation of alcohol at 2 and 25 °C. The practicality of the method is thus not restricted by temperature but by the competitive absorption of light between the crude oil and the sensitizer. Further work

is in progress on a sensitizer which will absorb at longer wavelengths.

Acknowledgment

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Analytical Method for Calculation of Deposition of Particles from Flowing Fluids and Central Force Fields in Aerosol Filters

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■ The methods applied for calculation of the deposition rate of particles depositing on a cylinder or in aerosol filters under the influence of external forces (limiting trajectories, Duchin and Deryaguin, and Natanson methods) are briefly discussed. By combining the Natanson method with dimensional analysis and with the concept of generalized (Friedlander's) variables, a new method is developed. This method not only enables the calculation of the deposition rate but in certain cases also enables the formulation of the general similitude law. Under certain assumptions about the flow field and field of external forces, the deposition of particles due to the simultaneous action of external forces and direct interception on a cylinder and in aerosol filters can be described by one single-valued function of one variable having a universal character for the treated two-mechanism problem. As an application example, the problem of deposition of Stokes finite size particles on a cylinder due to the action of attractive coulombic forces for the case of potential flow is solved.

One of the basic problems in the theory of aerosol filters is the determination of the deposition rate of particles Φ (number of particles deposited in unit time on the unit length of the cylinder transverse to the fluid flow). This rate can be expressed by

$$\Phi = 2an_0U_0E_{XR} \quad (1)$$

where a is the cylinder radius, n_0 is the number concentration of particles at infinite distance from the cylinder, U_0 is the fluid velocity at infinite distance, and E_{XR} is the capture coefficient of the cylinder due to the simultaneous action of mechanism X and direct interception. Deposition of monodisperse, spherical particles of radius r is treated as the deposition of point particles on a coaxial cylinder of radius $a+r$. Deposition of particles takes place on the part of the cylinder surface where the condition

$$v_\rho(\rho = a+r, \theta) \leq 0 \quad (2)$$

is satisfied, where ρ, θ are the polar coordinates (θ is measured from the positive x -axis), and $v_\rho(\rho, \theta)$ is the radial component of the particle velocity. Let us define the quantity θ_0 by

$$v_\rho(\rho = a+r, \theta = \theta_0) = 0 \quad (3)$$

so that θ_0 decides which part of the cylinder surface deposition occurs. Consequently, the limiting trajectory, separating the trajectories of depositing and not depositing particles, goes through the point $\rho = a+r, \theta = \theta_0$. It will be shown below that in the case of deposition due to the action of external forces and direct interception, Condition 2 is satisfied; consequently, deposition occurs in the range $\theta_0 \leq \theta \leq \pi$. In the case of pure direct interception, $\theta_0 = \pi/2$ so that deposition occurs in the range $\pi/2 \leq \theta \leq \pi$. Moreover, if there are attractive external forces between the particles and the cylinder, the part of the cylinder surface where the deposition occurs increases so that θ_0 decreases, being in the interval $0 \leq \theta_0 \leq \pi/2$. If the attractive interaction is sufficiently large, then $\theta_0 = 0$, and the deposition takes place on the whole cylinder surface $0 \leq \theta \leq \pi$. In the case of repulsion forces, the part of the cylinder surface where the deposition occurs decreases so that θ_0 increases, being in the interval $\pi/2 \leq \theta_0 \leq \pi$. If the repulsive interaction is sufficiently large, then $\theta_0 = \pi$, Condition 2 is never satisfied, and there will be no deposition.

For determination of the deposition rate Φ , essentially three methods have been developed, all based on the assumption that inertia of the particles can be neglected. Analytical formulation and justification of this assumption are dependent on the type of interaction between particles and the cylinder. The first and the oldest method follows.

Method of Limiting Trajectories

The motion equation of the inertialess particles with external forces $\vec{F}(\rho, \theta)$ is given by

$$\vec{V}(\rho, \theta) = \vec{U}(\rho, \theta) + B\vec{F}(\rho, \theta) \quad (4)$$

where \vec{V} is the vector of the particle velocity, \vec{U} is the vector of fluid velocity, and B is the particle mobility. Solution of the differential Equation 4 is $\rho = \rho(\theta, C)$, representing a system

of particle trajectories dependent on one parameter C (integration constant). This constant is determined from the condition for $\rho = a + r$, $\theta = \theta_0$, and $C = C_{lim}$. Hence, the equation of the limiting trajectory separating the depositing and penetrating particles is $\rho = \rho(\theta, C_{lim})$. Then the capture coefficient E_{XR} defined by Condition 1 is given by

$$E_{XR} = \frac{h}{a} = \frac{1}{a} \lim_{\substack{\rho \rightarrow \infty \\ \theta \rightarrow \pi}} \rho \sin \theta \quad (5)$$

where the quantity h represents the distance of the limiting trajectory from the axis of flow at infinite distance from the cylinder. (Quantity h is sometimes called the effective fiber radius.) In principle, this method can be applied for any flow field $\vec{U}(\rho, \theta)$ and any force field $\vec{F}(\rho, \theta)$. However, by use of this procedure, mathematical difficulties frequently arise, e.g., there are no analytical solutions, the degree of accuracy of the approximate analytical solutions is unknown, or there are only numerical or graphical solutions. Although this method can be combined with dimensional analysis, this approach gives no deeper insight into the more general correlations of the obtained results.

Duchin-Deryaguin Method

The basic assumption of this method is that the field of external forces is solenoidal, i.e.,

$$\text{div } \vec{F}(\rho, \theta) = \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho F_\rho) + \frac{1}{\rho} \frac{\partial F_\theta}{\partial \theta} = 0 \quad (6)$$

Duchin and Deryaguin (1) have shown that if Condition 6 is satisfied, then the concentration along the trajectories of particles is constant and the deposition rate is given by

$$\Phi = n_0 \iint (u_n + BF_n) dS \quad (7)$$

where u_n and F_n are the components of the vectors \vec{U} and \vec{F} normal to the collecting surface S . Integration in Condition 7 is carried out on the part of the collector surface where the deposition takes place. In the case of the cylinder, taking into account Conditions 2-4, Equation 7 becomes

$$\Phi = -2 n_0 (a + r) \int_{\theta_0}^{\pi} [u_\rho(\rho = a + r, \theta) + BF_\rho(\rho = a + r, \theta)] d\theta \quad (8)$$

This method was applied by Levin (2) for the description of deposition of charged particles on charged collectors (sphere, cylinder) due to coulombic forces, assuming that direct interception can be neglected. The second application of the Duchin-Deryaguin method was reported by Pich (3) for developing a theory of the gravitational mechanism of the action of fibrous filters including the direct interception. Unfortunately, the basic Condition 6 greatly reduces the possibilities of application of this method.

Natanson Method

Natanson (4) developed an effective method based on the assumption that the external forces are central, attractive, and depend only on the radial coordinate ρ so that $F_\rho(\rho, \theta) = 0$, $F_\theta(\rho, \theta) = -F(\rho)$. The basic idea of this method is as follows: The flow field around a cylinder is described by the stream function $\psi(\rho, \theta)$ related to the velocity components by $u_\rho = 1/\rho \partial\psi/\partial\theta$ and $u_\theta = -\partial\psi/\partial\rho$. Then the motion equation of the particle (Equation 4) written in polar coordinates and using the assumptions about the acting forces becomes

$$v_\rho = \frac{d\rho}{dt} = \frac{1}{\rho} \frac{\partial\psi}{\partial\theta} - BF(\rho) \quad (9)$$

$$v_\theta = \frac{\rho d\theta}{dt} = -\frac{\partial\psi}{\partial\rho}$$

where t is the time. From Equation 9 it follows the differential equation of the particle trajectory in the form

$$\frac{\partial\psi}{\partial\rho} d\rho + \frac{\partial\psi}{\partial\theta} d\theta = d\psi = B\rho F(\rho) d\theta \quad (10)$$

From the equation $\psi = \psi(\rho, \theta)$, variable ρ is expressed as $\rho = \rho(\psi, \theta)$ substituted into Equation 10, and the resulting differential equation is integrated. The integral of Equation 10 is $\psi = \psi(\theta, C)$ where C is an integration constant. For $\theta \rightarrow \pi$ the particle trajectory coincides with the flow line characterized by $\psi(\theta = \pi, C)$. From the physical properties of the stream function, it follows that the capture coefficient E_{XR} defined by Condition 1 is given by

$$E_{XR} = \frac{1}{aU_0} \psi(\theta = \pi, C_{lim}) \quad (11)$$

where C_{lim} is the value of C corresponding to the limiting trajectory. For the determination of C_{lim} two cases are distinguished, both exploiting Condition 2.

In the first case, Condition 2 is satisfied for any $0 \leq \theta \leq \pi$. Hence, $v_\rho(\rho = a + r, \theta = 0) \leq 0$. An equivalent expression of this condition is obtained using the first Equation 9 in the form

$$\frac{(a + r)BF(\rho = a + r)}{aU_0} \geq 1 \quad (12)$$

$$\left(\frac{\partial\psi}{\partial\theta} \right)_{\rho=a+r}^{\theta=0} \geq 1$$

As the point $\rho = a + r$, $\theta = 0$ lies on the axis of flow which is a streamline characterized by $\psi = 0$, the determining equation for C_{lim} is

$$\psi(\theta = 0, C_{lim}) = 0 \quad (13)$$

In the second case, Condition 2 is satisfied only for $\theta_0 \leq \theta \leq \pi$. The definition of θ_0 is given by Condition 3. An equivalent definition is obtained with the first Equation 9

$$\left(\frac{\partial\psi}{\partial\theta} \right)_{\rho=a+r}^{\theta=\theta_0} = (a + r)BF(\rho = a + r) \quad (14)$$

Then the determining equation for C_{lim} obtained from the solution of Equation 10 is

$$\psi(\rho = a + r, \theta = \theta_0) = \psi(\theta = \theta_0, C_{lim}) \quad (15)$$

Hence, the problem is solved by Equation 11 where C_{lim} is given by Equations 13 or 15 and θ_0 is defined by Equation 14.

The advantage of this method is that the calculation is straightforward, and there is no need to calculate the limiting particle trajectory. Furthermore, the necessary condition for application of this method (central external forces) is not so restrictive as the corresponding condition (solenoidal external forces) required for the application of the D-D method.

The disadvantage of this method, in the author's opinion, is that this approach was not combined with the dimensional analysis. Another drawback of Natanson's paper (again the author's opinion) is that Natanson did not derive explicit expressions for the capture coefficient E_{XR} in the case $\theta_0 \neq 0$ for different types of electrostatic and molecular interactions between particles and the cylinder. As nobody derived these explicit expressions, the theory of the electrostatic and molecular mechanism of action of fibrous aerosol filters is incomplete. Moreover, there is a certain kind of confusion, especially when Natanson's results are treated and compared with the results of other authors. This can be checked by comparing the textbooks of Pich (5), Hidy and Brock (6), and Davies (7) with the original Natanson paper.

The aim of this paper is to generalize the Natanson method by consistent application of the dimensional analysis and to use the Friedlander concept of generalized variables. With this approach an approximate but analytic and clear theory of the electrostatic and molecular mechanism of action of fibrous aerosol filters can be developed.

Theory

All known flow fields around an isolated cylinder and in the system of cylinders used in the theory of aerosol filters can be expressed as (8)

$$\psi(\rho, \theta) = \frac{aU_0}{2H} f(\rho) \sin \theta \quad (16)$$

where $f(\rho)$ is the given function for the given type of flow, and H is a hydrodynamic factor which is a constant (potential flow), dependent on the Reynolds number (Lamb's velocity field), or dependent on the filter porosity (Kuwabara, Happel, and reduced Spielman-Goren velocity fields). If the external forces are absent $\vec{F}(\rho, \theta) = 0$, then from Condition 4 $\vec{V}(\rho, \theta) = \vec{U}(\rho, \theta)$ and the trajectories of particles coincide with the flow lines. In this case, corresponding to pure direct interception, Condition 2 using 16 becomes

$$v_\rho(\rho = a + r, \theta) = u_\rho(\rho = a + r, \theta) = \frac{aU_0}{2H(a+r)} f(\rho = a+r) \cos \theta \leq 0 \quad (17)$$

As always $\psi(\rho, \theta) \geq 0$, Condition 17 is satisfied for $\pi/2 \leq \theta \leq \pi$, and the deposition occurs only in this range. From Condition 3 using 17, it follows $\theta_0 = \pi/2$, and the capture coefficient due to pure direct interception E_R is given by

$$E_R = \frac{1}{aU_0} \psi(\rho = a + r, \theta = \pi/2) = \frac{1}{2H} f(\rho = a + r) \quad (18)$$

[The equation of the streamline is $\psi = \text{const} = K$, and the value of K gives the amount of fluid flowing in unit time through unit height cross-section given by $\psi = K$ and $\psi = 0$. From Equation 16 it follows that the streamline $\psi = 0$ corresponds to the axis of flow $\theta = 0$ so that Equation 18 is immediately obtained.] Equation 18 contains the whole theory of the direct interception mechanism provided that the flow field (Equation 16) is known. Let us define the dimensionless polar coordinate $\rho^* = (\rho - a)/a$ and the dimensionless stream function $\psi^*(\rho^*, \theta)$ by

$$\psi^*(\rho^*, \theta) = \frac{1}{aU_0 E_R} \psi(\rho^*, \theta) = \frac{1}{2HE_R} f(\rho^*) \sin \theta = \frac{f(\rho^*)}{f(\rho^* = N_R)} \sin \theta \quad (19)$$

where Equations 16 and 18 were applied and $N_R = r/a$ is the parameter of direct interception. Corresponding dimensionless fluid velocity components $u_\rho^* = u_\rho/U_0$, $u_\theta^* = u_\theta/U_0$ are related to the function ψ^* by

$$u_\rho^* = \frac{1}{1 + \rho^*} E_R \frac{\partial \psi^*}{\partial \theta}, \quad u_\theta^* = -E_R \frac{\partial \psi^*}{\partial \rho^*} \quad (20)$$

Assuming that the forces acting on the particle are central, attractive and dependent only on the radial coordinate ρ (central potential forces) so that $F_\rho(\rho, \theta) = -F(\rho)/\rho$ and $F_\theta(\rho, \theta) = 0$, the motion Equation 4 in polar dimensionless coordinates ρ^*, θ becomes

$$v_\rho^* = \frac{d\rho^*}{dt^*} = \frac{1}{1 + \rho^*} E_R \frac{\partial \psi^*}{\partial \theta} - \frac{B/F(\rho^*)}{U_0} \quad (21)$$

$$v_\theta^* = (1 + \rho^*) \frac{d\theta}{dt^*} = -E_R \frac{\partial \psi^*}{\partial \rho^*}$$

where $t^* = U_0 t/a$ is a dimensionless time. From Equation 21 it follows

$$\frac{\partial \psi^*}{\partial \rho^*} d\rho^* + \frac{\partial \psi^*}{\partial \theta} d\theta = d\psi^* = \frac{(1 + \rho^*)B/F(\rho^*)}{U_0 E_R} d\theta \quad (22)$$

Condition 2 in dimensionless form and using Equations 19 and 21 becomes

$$v_\rho^*(\rho^* = N_R, \theta) = \frac{1}{1 + N_R} E_R \cos \theta - \frac{B/F(\rho^* = N_R)}{U_0} \leq 0 \quad (23)$$

As both N_R and E_R are not negative, Condition 23 can be expressed

$$\cos \theta - x_F \leq 0 \quad (24)$$

where

$$x_F = \frac{(1 + N_R)B/F(\rho^* = N_R)}{U_0 E_R} \quad (25)$$

is a positive dimensionless complex (first Friedlander's coordinate). Substitution of Equation 25 into 22 gives

$$d\psi^* = \frac{(1 + \rho^*)}{(1 + N_R)} \frac{F(\rho^*)}{F(\rho^* = N_R)} x_F d\theta \quad (26)$$

In order to formulate the general similitude law, let us assume that

$$M(\rho^*, N_R, x_F) = \frac{(1 + \rho^*)/F(\rho^*)}{(1 + N_R)/F(\rho^* = N_R)} x_F = N(\psi^*, \theta, x_F) \quad (27)$$

i.e., the right-hand side of Equation 26 can be expressed, using Equation 19, as a function of variables ψ^*, θ with parameter x_F . Validity of this assumption is dependent on the type of force and flow field around the cylinder. If Equation 27 is satisfied, then the integral of Equation 26 is $\psi^* = \psi^*(x_F, \theta, C)$ where C is the integration constant. Using this solution, Equation 19, and taking into account that $\psi(\rho^* \rightarrow \infty, \theta \rightarrow \pi) = hU_0$ where h is related to E_{XR} by Equation 5 it is obtained

$$y_F = \frac{E_{XR}}{E_R} = \psi^*(x_F, \theta = \pi, C) \quad (28)$$

where y_F is used as a second Friedlander's coordinate. For the determination of C in Equation 28, Condition 24 is applied. Two cases are distinguished.

$x_F \geq 1$. In this case, Condition 24 is satisfied for any $0 \leq \theta \leq \pi$. Hence, the deposition occurs over the whole cylinder surface, and the limiting trajectory goes through the point $\rho^* = N_R, \theta = 0$. Then from Equation 10 it follows $\psi^*(\rho^* = N_R, \theta = 0) = 0 = \psi^*(x_F, \theta = 0, C)$. Hence, the determining equation for C in this case is

$$\psi^*(x_F, \theta = 0, C) = 0 \quad (29)$$

From Equation 29 it follows that $C = C(x_F)$. Substitution of this result into Equation 28 yields the similitude law

$$y_F = \frac{E_{XR}}{E_R} = \psi^*[x_F, \theta = \pi, C(x_F)] = y_F(x_F) \quad (30)$$

$x_F < 1$. In this second possible case from Equation 24, it follows that there is an angle $0 \leq \theta_0 \leq \pi/2$ defined by $\cos \theta_0 - x_F = 0$ so that $\theta_0 = \arccos x_F$. Hence if x_F increases from 0 to 1, the angle θ_0 decreases from $\pi/2$ to 0, and the deposition range increases. From Equation 24 it can be easily deduced that the deposition occurs in the range $\theta_0 \leq \theta \leq \pi$ so that the limiting trajectory goes through the point $\rho^* = N_R, \theta = \theta_0$. Then from Equation 19 it follows $\psi^*(\rho^* = N_R, \theta = \theta_0) = \sin \theta_0 = \psi^*(x_F, \theta = \theta_0, C)$ and because $\sin \theta_0 = (1 - \cos^2 \theta_0)^{1/2} =$

$(1 - x_F^2)^{1/2}$, the determining equation for C becomes

$$\psi^*(x_F, \theta = \theta_0 = \arccos x_F, C) = (1 - x_F^2)^{1/2} \quad (31)$$

Evidently, for $\theta_0 = 0$ is $x_F = 1$ and Equation 31 reduces to Equation 29. Furthermore, from Equation 31 it follows that also in this case $C = C(x_F)$, and the similitude law (Equation 30) is also valid in this case. Consequently, the similitude law (Equation 30) is of general character being valid for arbitrary $0 \leq x_F < \infty$.

Summarizing the problem is solved by Equation 28 where C is determined by Equation 31 for $x_F < 1$ and by Equation 29 for $x_F \geq 1$.

It can be easily shown that the resulting equations of the Natanson method are special cases of the present theory. By use of Equations 16, 18, and 19, it can be proved that Equation 11 is a special case of Equation 28, Condition 12 is equivalent to $x_F \geq 1$, Equation 13 is a special case of Equation 29, Equation 14 is equivalent to $\cos \theta_0 = x_F$, and Equation 15 is a special case of Equation 31.

The case of repulsion forces acting between the particle and the cylinder can be treated in a similar way. Let us assume that these repulsion forces are central and dependent only on the radial coordinate ρ so that $F_r(\rho, \theta) = +F(\rho)/\rho$ and $F_\theta(\rho, \theta) = 0$. Then using Equations 4, 19, and 20, Condition 2 becomes

$$\cos \theta + x_F \leq 0 \quad (32)$$

where x_F is again given by Equation 25. From Equation 4, following the same approach as in the previous case, it follows

$$d\psi^* = -\frac{(1 + \rho^*)/F(\rho^*)}{(1 + N_R)/F(\rho^* = N_R)} x_F d\theta \quad (33)$$

If Condition 27 is satisfied, then the solution of Equation 33 can be expressed as $\psi^* = \psi^*(x_F, \theta, C)$ and

$$y_F = \frac{E_{XR}}{E_R} = \psi^*(x_F, \theta = \pi, C) \quad (34)$$

For the determination of the integration constant C , two cases are again distinguished.

$x_F \geq 1$. Condition 32 is satisfied in this case only for $x_F = 1$ so that $\theta = \pi$. Hence, the limiting trajectory goes through the point $\rho^* = N_R, \theta = \pi$. Then from Equation 19 it follows $\psi^*(\rho^* = N_R, \theta = \pi) = \psi^*(x_F, \theta = \pi, C) = 0$. With Equation 34, it is obtained

$$y_F = \frac{E_{XR}}{E_R} = 0 \text{ for } x_F \geq 1 \quad (35)$$

$x_F \leq 1$. In this second possible case from Condition 32 it follows that there is an angle $\pi/2 \leq \theta_0 \leq \pi$ given by $\theta_0 = \arccos(-x_F) = \pi - \arccos x_F$, and Condition 32 is satisfied only for $\theta_0 \leq \theta \leq \pi$. Consequently, the limiting trajectory goes through the point $\rho^* = N_R, \theta = \theta_0 = \pi - \arccos x_F$, and the determining equation for C obtained from Equations 19 and 34 becomes

$$\psi^*(x_F, \theta = \theta_0 = \pi - \arccos x_F, C) = (1 - x_F^2)^{1/2} \quad (36)$$

For $x_F = 1$ Equation 36 reduces to Equation 35. Furthermore from Equation 36 it follows $C = C(x_F)$. Substitution of this expression into Equation 34 yields the similitude law

$$y_F = \frac{E_{XR}}{E_R} = \psi^*[x_F, \theta = \pi, C(x_F)] = y_F(x_F) \quad (37)$$

Hence, the problem is solved by Equation 34 where C is determined by Equation 36 for $x_F \leq 1$ and by Equation 35 for $x_F \geq 1$.

From the developed theory, it follows that the case $x_F = 0$ corresponds to pure direct interception for which $y_F = E_{XR}/E_R = 1$. This can be easily proved using Equations 18, 24, and

26 in the case of attraction forces and using Equations 18, 32, and 33 in the case of repulsion forces.

Influence of the complex x_F on the magnitude of the deposition ranges on the cylinder surface is illustrated by Figure 1.

As an illustration of the application of the developed method, let us calculate the deposition of monodisperse, charged particles on a charged cylinder from the potential flow. Assuming the pure attractive coulombic interaction, then (4)

$$F_r(\rho, \theta) = -F(\rho)/\rho = -\frac{2/qQ}{\rho}, F_\theta(\rho, \theta) = 0 \quad (38)$$

where q is the particle charge and Q the charge per unit length of the cylinder. This force is central and potential so that the method can be applied. Potential flow field around the cylinder is described by (5)

$$\psi(\rho, \theta) = aU_0 \left(\frac{\rho}{a} - \frac{a}{\rho} \right) \sin \theta \quad (39)$$

so that Equation 16 is also satisfied. By use of Equation 39, Equation 18 yields

$$E_R = 1 + N_R - \frac{1}{1 + N_R} \quad (40)$$

Parameter x_F defined by Equation 25 using Equation 38 becomes

$$x_F = \frac{2/qQ/B}{aU_0 E_R} \quad (41)$$

Equation 26 using Equation 38 becomes $d\psi^* = x_F d\theta$ so that Condition 27 is also satisfied. Primitive integration of this equation gives $\psi^* = x_F \theta + C$. Equation 28 yields

$$y_F = \pi x_F + C \quad (42)$$

Application of Equation 31 to 42 gives $C = (1 - x_F^2)^{1/2} - x_F \arccos x_F$ for $x_F \leq 1$, and application of Equation 29 yields $C = 0$ for $x_F \geq 1$. Substitution of these expressions into Equation 42 gives the solution of the problem expressed in generalized variables

$$y_F = x_F(\pi - \arccos x_F) + (1 - x_F^2)^{1/2} \text{ for } x_F \leq 1 \quad (43a)$$

$$y_F = \pi x_F \text{ for } x_F \geq 1 \quad (43b)$$

If there is no coulombic interaction, i.e., $q = 0$ or $Q = 0$, then

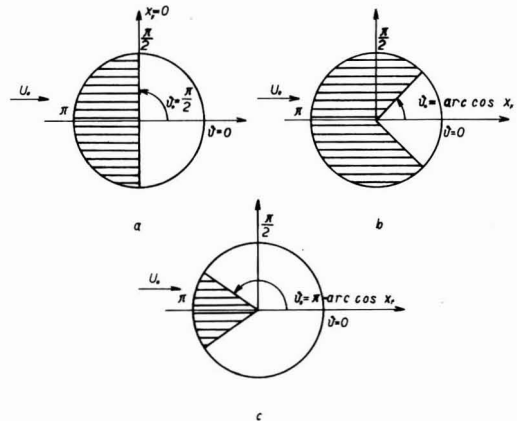


Figure 1. Deposition ranges on cylinder surface in cases of (a) pure direct interception, (b) direct interception and attractive interaction, (c) direct interception and repulsive interaction

Equation 41 gives $x_F = 0$, and Equation 43a gives $y_F = E_{NR}/E_R = 1$ so that E_{NR} is reduced to E_R given by Equation 40. For $x_F = 1$ both Equations 43a and 43b give $y_F = \pi$. Finally, for $x_F \geq 1$, Equation 43b reduces to $E_{NR} = 2\pi/QQ/B/aU_0$ which is independent of N_R . Consequently, for $x_F \geq 1$, deposition of finite size particles occurs with the same rate as that of point particles.

The developed method can be treated as the development of the idea originally suggested by Friedlander (9) who investigated the simultaneous action of diffusion and direct interception so that the deposition mechanism X was represented by diffusion and consequently $E_{NR} = E_{DR}$. He concluded that instead of expressing the results in the usual form $E_{DR} = E_{DR}(N_D, N_R)$ where $N_D = Pe^{-1}$ (Pe is the Péclet number), i.e., obtaining a system of curves dependent on one parameter, it is advantageous to select more general variables than the usual dimensionless parameters ($x_F = N_R Pe^{1/3}$, $y_F = E_{DR} Pe N_R$) in such a way that in terms of these variables the functional dependence $E_{DR} = E_{DR}(N_D, N_R)$ can be expressed as a single valued function of one variable, i.e., $y_F = y_F(x_F)$.

The significance of this idea was recognized by Natanson and Ushakova (10) who first applied the term "Friedlander's coordinates" and raised the problem of uniqueness of selection of the coordinates x_F, y_F . This problem was solved again by Friedlander (11) by deriving the similitude law $y_F = y_F(x_F)$ for the simultaneous action of diffusion and interception

mechanisms. The present treatment extends this approach to other two-mechanism problems where the mechanism X is not represented by diffusion but by the action of central force. This is the case in different kinds of electrostatic interactions and in the London-Van der Waals interaction. Hence, the present treatment serves as a methodical basis for developing an analytical theory of electrostatic and molecular mechanisms of filtration.

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Characterization of Aza-Arenes in Basic Organic Portion of Suspended Particulate Matter

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■ Aza-arenes, formed as trace pollutants by incomplete combustion of N -containing organic matter, are found in the basic fraction of New York City's suspended particulate matter. We describe an isolating technique utilizing extraction, solvent partitioning, and a sequence of chromatographic separations. Particulate matter collected on filters is Soxhlet extracted with benzene/methanol, and the basic fraction derived from the extractable matter is pre-fractionated by HPLC. The subfractions are further separated by GC/MS and HPLC, followed by spectroscopic identification. This approach leads to the unambiguous identification of over 20 aza-arenes and other N -bases previously unidentified, and gives insight into the complexity of the basic fraction. Quantitative data also show an unanticipated abundance of quinolines, isoquinolines, and their alkyl derivatives in the fraction.

Analytical methods for polynuclear aza-heterocyclic hydrocarbons (aza-arenes) have received some attention in the past, since a number of these compounds, such as dibenz(a,j)acridine, dibenz(a,h)acridine, and some alkyl benzacridines, are known animal carcinogens (1, 2). Recently,

quinoline has been found to induce hepatomas in rats (3). Although bioassays on aza-arenes have been few, it is suspected that many of these compounds might have tumorigenic activity (2). Aza-arenes are formed, as trace pollutants, during incomplete combustion of nitrogen-containing substances and are therefore found in urban suspended particulate matter (4, 5), tobacco smoke (6, 7), automobile exhausts (8), and many pollution source effluents (9).

Separation methods for aza-arenes have been well documented. They have been separated by thin-layer chromatography (TLC) (10), paper chromatography (11), electrophoresis (12), and conventional liquid chromatography using adsorption (13) and ion-exchange packings (14). Gas chromatography (GC) has also been successfully applied with a flame ionization detector (15) or with mass spectrometry as a specific ion detector (4). Various modes of high-pressure liquid chromatography, including reversed phase (16), adsorption (16), complexation (17), and liquid-liquid partitioning (18) have also been used for the separation of aza-arene standard compounds.

Aza-arenes, with the exception of neutral indole and carbazole homologs, are found in the basic organic fraction of suspended particulate matter. Although, in general, this fraction only constitutes a small percentage (0.5–3%) of the organic matter (19), bioassay data have shown the basic fraction to be carcinogenic to infant mice when administered subcutaneously (20). Sawicki and coworkers identified aza-

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arenes in the basic fraction after chromatographic enrichment by spectroscopic and spectrofluorimetric means (5, 9). Nineteen aza-arenes (10 parent ring compounds and 9 alkyl derivatives) were found in a Nashville sample (5). These procedures yield semiquantitative data and were most helpful in the past, although they may lead to composite quantitative results for several aza-arenes.

More recently, modern analytical instrumentation has been used to recheck earlier results. Alberini et al. (15) identified 11 aza-arenes in the basic fraction of suspended particulate matter by retention times on glass capillary columns. Using a different approach, Brocco et al. employed a TLC-GC method and identified seven aza-arenes, including quinoline which had not been previously identified (21). The results of the two studies were quite different from those reported by Sawicki et al., but since identifications were based solely on GC retention times, their data were questionable. Very recently, Cautreels and Van Cauwenbergh reported a detailed study of the basic fraction by mass fragmentography (4). Fifteen aza-arene compound types were identified in an Antwerp air particulate sample. Each type contains many isomers, undistinguishable by mass spectrometry.

Frei et al. (22) attempted to measure aza-arenes in the air particulate matter by injecting untreated particulate extracts into a silver-impregnated column in their HPLC system. However, no aza-arene peak was identifiable from the chromatogram.

In our approach, we prefractionate the basic fraction by HPLC into nine subfractions and characterize each subfraction independently by GC/MS and HPLC reversed phase followed by UV and fluorescence spectroscopy of the isolated peak. In view of the complexity of the basic fraction, we believe that this approach offers the most reliable qualitative and quantitative analysis of aza-arenes and other unknown components in the fraction. Since mass spectra of isomeric aza-arenes, e.g., phenanthridine and benzo(f)quinoline, are identical, the use of UV and fluorescence techniques supplements GC/MS and gives unambiguous identification and quantitation of these isomers.

Experimental

The experimental procedure is outlined in Figure 1.

Reagents. Reference compounds were obtained from K&K, Aldrich Chemical Co., and Pfaltz & Bauer. 4-Azapyrene, 2-aza-fluoranthene, 13-azafluoranthene, 11H-indeno(1,2-b)quinoline, and four dimethylquinolines were kindly donated by Dr. Sauerland of the Rütgerswerke AG, Duisburg, West Germany. All solvents used were spectrograde from Fisher Scientific or from Burdick & Jackson.

Sampling. Particulate matter samples were provided by the New York City Department of Air Resources. They were collected at various sites in New York City's aerometric network on glass fiber filters by use of high-volume samplers. The average rate of sampling is 40–50 ft³/min. The weight of a 24-h sample ranges from 90 to 200 mg depending on site, season, and weather conditions. Sample 1 is a 180-filter combined sample collected during February–April 1975, randomly selected from different stations. Sample 2 is a similar 100-filter sample collected during January–March 1975. The two samples were supplied separately from the Department of Air Resources.

Extraction. Extraction from soiled filters was carried out for 8 h in two large soxhlet extraction apparatus with preextracted Whatman cellulose thimbles (123 × 43 mm, Fisher Scientific). Each thimble accommodates five filters. Benzene/methanol (4:1) was used as the extracting solvent (23). (Since the azeotropic mixture is 60.5:39.5, the actual extracting solvent in the soxhlet apparatus may not be 4:1.) Other workers have used CHCl₃ (5), benzene (4, 21), or cyclohexane

(15). We chose this solvent because it gives the highest amount of extractable organic matter and yields the most biologically active extract (19). We also believe that since aza-arenes are weak bases, and salt formation with inorganic and organic acids on the filter is a possibility, a polar solvent must be used.

Partitioning. The extract was evaporated to near dryness in a rotary evaporator at water bath temperatures under 45 °C, redissolved in 100 mL CHCl₃, and partitioned twice with equal volumes of water. The aqueous layer containing the water-soluble compounds was discarded. The CHCl₃ layer was extracted twice with 10% H₂SO₄ and once with 20% H₂SO₄ solution. The use of a strong acid is recommended since aza-arenes are weak bases. Emulsions were often encountered in these partitioning steps but could be minimized by sonicating in an ultrasonic bath. The acidic layers were combined, cooled in an ice bath, and neutralized by adding saturated NaOH solution until pH 12 was reached. This solution (ca. 300 mL) was then back-extracted three times into equal volumes of CHCl₃. The combined CHCl₃ solution was dried over anhydrous Na₂SO₄, filtered, and concentrated to 0.1 mL. The resulting dark brown solution, the basic fraction of particulate organic matter, contained aza-arenes and other N-bases.

Prefractionation. A prefractionation step is necessary since the basic fraction, especially when derived from a benzene/MeOH extraction, is too complex for any single separation technique. A high-pressure liquid chromatograph Model ALC/GPC 202 (Waters Associates) equipped with Model M-6000 pumps, Model 660 solvent programmer, and a 254-nm differential UV detector was used. Lichrosorb SI 60 silanized (30 μ diameter) (Brinkman Instruments, Inc.) was dry packed into a 2.1 mm i.d. × 60 cm stainless steel column for the prefractionation. Figure 2 shows a typical prefractionation chromatogram. With a solvent composed of 0.5% propanol-2 in *n*-hexane and a flow rate of 3.0 mL/min, most aza-arenes will elute between 4–25 min. Fifteen minutes after the injection of an 100-μL aliquot of the basic fraction, the solvent composition was linearly programmed to 20% propanol-2 in CHCl₃ in 20 min. Eight subfractions (10–50 mL) were collected, concentrated, and redissolved in 100 μL of MeOH.

GC/MS Analysis. Aliquots of these subfractions were injected into a Hewlett-Packard Model 5982 dual source combined GC/MS system interfaced with a Hewlett-Packard Model 5933A computerized data system. Mass spectra were obtained by electron impact at 70 eV. A 10-ft, 1/8-in. o.d. stainless steel column, packed with 6% Dexsil 300 GC on Chromosorb W(HP), 80/100 mesh, was used at 60 mL/min

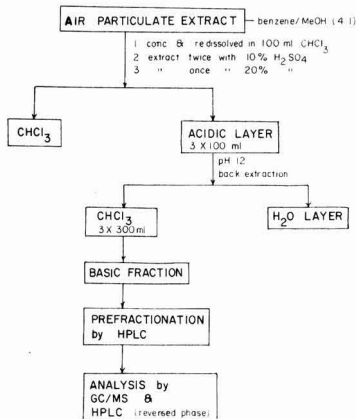


Figure 1. Analytical scheme for characterization of basic fraction of suspended particulate matter

flow rate. Temperature programming from 160 to 300 °C at 8 °C/min was initiated immediately after injection of each sample. Under these conditions the retention time of dibenz(a,h)acridine was 60 min. Other gas chromatograms were obtained on a Hewlett-Packard 5701A gas chromatograph with dual columns and flame ionization detectors.

HPLC Reversed-Phase Analysis. A 30 cm × 4 mm i.d. μ -Bondapak/C₁₈ reversed-phase column (Waters Assoc.) was used on the same HPLC described above. A solvent gradient from 20% CH₃CN/H₂O to 80% CH₃CN/H₂O at 4%/min and at a 3.0-mL/min flow rate was found to give satisfactory separation of most aza-arenes in 20 min. The chromatographic behavior of aza-arenes on reversed-phase columns is similar to that of the polynuclear aromatic hydrocarbons (24, 25) and is governed primarily by the number of aromatic rings.

Injections of 1–2% of the subfraction were sufficient for good HPLC chromatograms. However, use of over 30% of the subfraction was necessary when effluent fractions were to be analyzed by UV. Fractions (about 1 mL) sufficient to fill a UV microcell (4 × 10 mm) were taken. A Cary 14 UV-VIS spectrophotometer and a Perkin-Elmer MFP-2A spectrofluorometer were used to obtain spectra. Reference spectra were either obtained from aza-arene standards or from literature (26).

Extraction of 10 unexposed filters (blanks) and subsequent analysis by the same procedure yielded no aza-arenes.

Results and Discussion

Difficulties in This Analysis. The concentrations of aza-arenes in urban air ranged from 10 to 100 ng/g of the organic particulate extracts (10–100 ppb), roughly 100 times lower than the concentration of benzo(a)pyrene. The total amount of individual aza-arenes isolated rarely exceeded a few μ g even after sampling large volumes of air. The analysis of these trace quantities in a complex environmental matrix presents several difficulties. In the past these problems were partially circumvented by relying heavily on fluorescence techniques which are very selective methods for identifying aza-arenes. However, we believe that our approach, using two separate high-resolution chromatographic methods followed by a battery of spectroscopic techniques, gives the most detailed and unequivocal characterization of the basic fraction.

Sample contamination is another problem in trace analyses. All glassware was washed in chromic acid, thoroughly rinsed with water, and triply rinsed with spectrograde solvent. Trace contaminants in TLC and conventional LC packings are avoided completely by using a HPLC adsorption pre-fractionation. This step gives quantitative recovery and is extremely reproducible as well as convenient. The entire pre-fractionation can be completed in 1 h, and cut-off points between fractions are easily determined by the UV monitor (Figure 2). Silanized silica, a weaker adsorbent than regular silica, was used to prevent any possible irreversible adsorption of the sample.

Sample Size. In our study, over 100 filters were used for detailed analyses. For routine analysis of major aza-arenes, a sample size of 10 filters should be quite sufficient.

GC/MS of Subfractions. The use of a computerized data system greatly enhances the power of a GC/MS system. It simplifies data handling and allows convenient mass spectral background subtraction. It enables the use of mass fragmentography or specific ion monitoring, which has become a powerful tool for routine analysis and sample screening. Also, the use of a mass spectral search system greatly facilitates mass spectral comparisons and, therefore, the identification of unknowns.

It should be indicated that many components of the basic fraction are only tentatively identified or unidentified even

after rigorous efforts in searching reference mass spectra in the literature (27) and in our Hewlett-Packard disc reference library. The acute lack of reference mass spectral data, especially in the field of air pollution, is still a major hindrance to a more complete characterization. Fortunately, the aza-arenes as a class give very characteristic fragmentation patterns and are quite easily recognizable. Under electron impact, they yield strong molecular ion peaks and usually M-27 or M-28 peak corresponding to the loss of HCN or H₂CN fragments (28). The mass spectrum of quinoline shown in Figure 3 is quite representative of other aza-arenes and almost identical to the mass spectrum of isoquinoline. The mass spectrum of quinoline, isolated from Sample 1, Fraction IV, is very similar to that of pure quinoline (Figure 3). This is important in quantitative analysis by GC since one peak often contains composite components. Figures 4–6 are gas chromatograms of Fractions III, IV, and IVa, respectively. Most labeled peaks were identified by both retention time and by mass spectral data.

Specific Ion Monitoring. Figure 7 demonstrates the use of mass fragmentography on Fraction IV and shows the simultaneous monitoring of quinolines, isoquinolines, and many

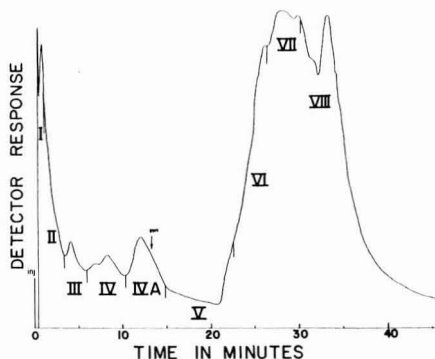


Figure 2. Typical HPLC pre-fractionation trace. Lichrosorb SI 60 column, 3.0 mL/min, 0.5 propanol-2 in hexane programmed after "RUN" to 20% propanol-2 in CHCl₃ in 20 min, sensitivity setting at non-linear

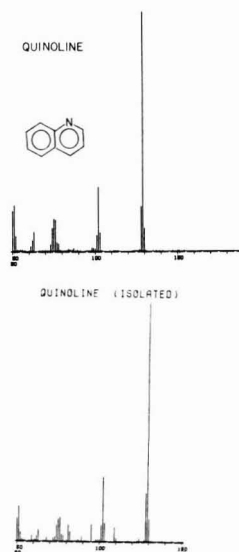


Figure 3. Mass spectra of pure quinoline and quinoline isolated in Sample 1

alkyl quinolines in the sample. The traces are normalized with respect to the quinoline peak. The relative concentration of each alkyl quinoline can be estimated from its total integrated area under each chromatographic peak. Figure 7 illustrates isoquinoline eluting after quinoline and shows the surprisingly high concentration of dimethylquinolines in New York City air (c.f., methylquinolines). The C₃-alkyl quinoline certainly would have escaped detection without the use of this technique.

HPLC. Figures 8–10 are HPLC chromatograms on Sub-fractions III, IV, and IVA, respectively. Most labeled peaks are identified by retention times, UV, and fluorescence spectra on the collected fractions. Compared to the GC traces (Figures 4–6), HPLC gives cleaner traces since the UV detector is quite sensitive to aza-arenes which have molar absorptivities of 10⁴–10⁵ at 254 nm. The detection limit for most aza-arenes is ≈ 1 ng (16) which compares favorably with that of GC, especially for the 5-ring, high boiling aza-arenes, e.g., dibenzacridines.

UV and Fluorescence Spectra. Figure 11 shows a UV spectrum of isoquinoline isolated from Fraction IVA of Sample 1. The dotted line is the spectrum from the pure compound at similar concentration taken from the literature (26). Figures 12 and 13 are similar fluorescence and excitation spectra of isolated benzo(f)quinoline. The spectra are not

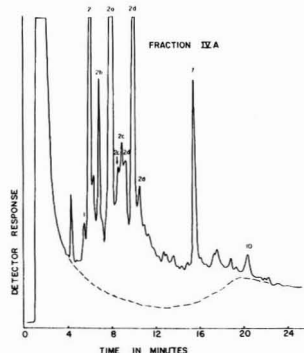


Figure 6. Gas chromatogram of Fraction IVA of Sample 1
Chromatographic conditions same as in Figure 3

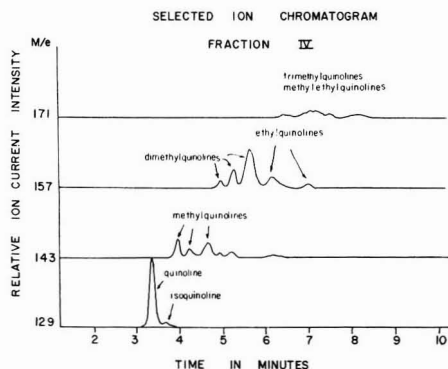


Figure 7. Selected ion chromatograms on Fraction IV, quinoline fraction
Chromatographic conditions same as in Figure 4

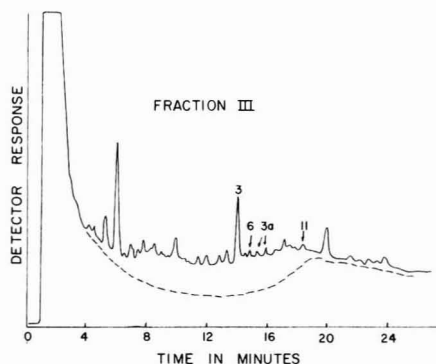


Figure 4. Gas chromatogram of Fraction III of Sample 1
Chromatographic conditions: 160 °C programmed to 300 °C at 8 °C/min, helium flow rate 30 mL/min, hydrogen pressure 20 psi, air pressure 30 psi. Column = 10-ft, 1/8-in., 6% Dexsil 300 GC on Chromosorb W(HP), 80/100 mesh; sensitivity = X80. Numbers correspond to compounds listed in Table I

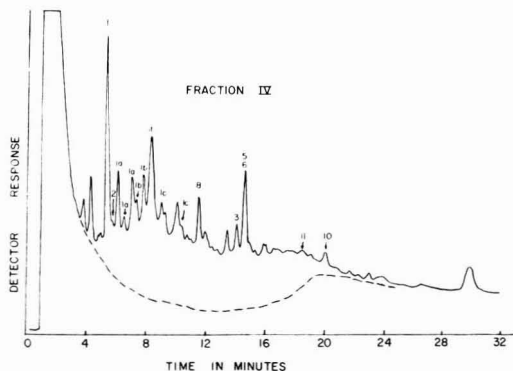


Figure 5. Gas chromatogram of Fraction IV of Sample 1
Chromatograph conditions same as in Figure 3

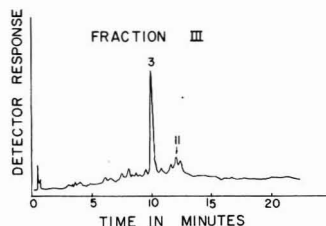


Figure 8. Liquid chromatogram of Fraction III of Sample 1
Chromatographic conditions: 20% CH₃CN in H₂O programmed to 80% CH₃CN in H₂O at 4%/min at 3.0 mL/min flow rate; column: μ-Bondapak/C18; sensitivity = 0.2 full-scale absorbance unit. Numbers correspond to compounds listed in Table I

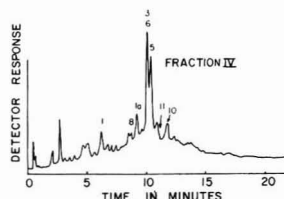


Figure 9. Liquid chromatogram of Fraction IV of Sample 1
Chromatographic conditions same as in Figure 8

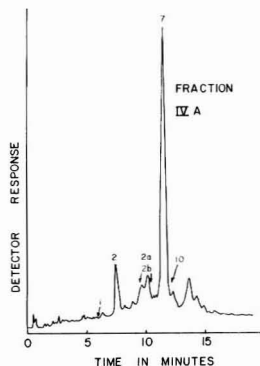


Figure 10. Liquid chromatogram of Fraction IVA of Sample 1
Chromatographic conditions same as in Figure 8

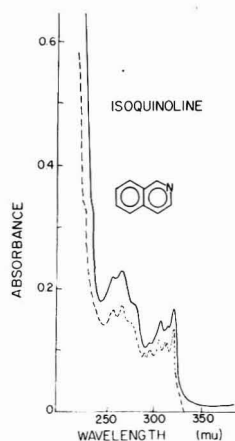


Figure 11. UV spectrum of isoquinoline isolated in Sample 1

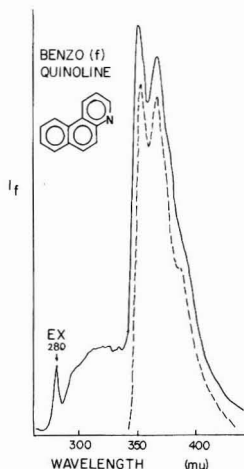


Figure 12. Fluorescence spectrum of benzo(f)quinoline isolated in Sample 2

Excitation slit width, 4 nm; emission slit width, 4 nm

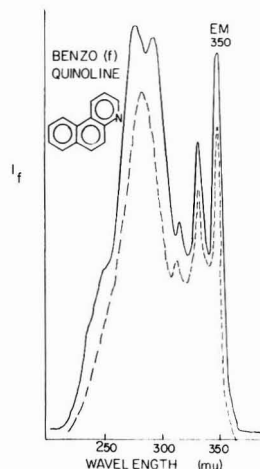


Figure 13. Excitation spectrum of benzo(f)quinoline isolated in Sample 1

Excitation slit width, 4 nm; emission slit width, 4 nm

corrected for source intensity and detector wavelength response variations.

Quantitation. Quantitative data on Samples 1 and 2 were obtained as follows: Two synthetic mixtures of aza-arene reference compounds were carefully prepared. An aliquot of these solutions was injected routinely to generate retention data and to check column reproducibility. The area under each peak was compared to that derived from an aliquot injection of a sample subfraction solution, usually after its identity and purity had been assured by mass spectrometry. Isomers like phenanthridine and benzo(f)quinoline were quantitated from UV spectra of collected fractions separated by HPLC.

Concentrations of Aza-Arenes in New York City Suspended Particulate Matter. The concentrations of aza-arenes and other *N*-bases from the basic fraction are summarized in Table I.

2-Ring Aza-Arenes. Quinolines escaped identification by Sawicki et al. since they possess low molar absorptivity (3.8×10^3 at 308 nm) and do not fluoresce. We have confirmed Cautreels and Van Cauwenberghe's finding (4) by independently discovering quinoline in our New York City samples, and have extended their observations by demonstrating with quantitative data the complexity of the quinoline (IV) and isoquinoline (IVA) fractions. In our two New York City samples, the concentration of isoquinoline exceeds that of quinoline by 3-7 times. The highest concentration of aza-arenes (310 ng/1000 m³ in Sample 1) is associated with a methyl derivative of isoquinoline. The exact structure has not yet been determined because of the lack of a reference compound; however, boiling point data (29) suggest its identity to be a 5- or 8-methylisoquinoline. It is possible that there are very specific precursors for this compound.

It should be emphasized that the reported levels of quinolines and isoquinolines represent the minimum concentrations in ambient air because quinoline (bp 237 °C) and isoquinoline (bp 242 °C) are probably not quantitatively trapped by the high-volume samplers. Their retention on glass fiber filters might be correlated to their hygroscopicity or possibly to their basicity.

3-Rings. Of the five isomers of 3-ring aza-arenes, benzo(f)-isoquinoline has the highest concentration (three times that of acridine in Sample 1) in our samples. This compound has



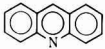




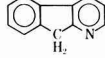
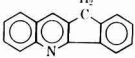

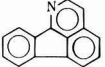

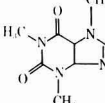
not been previously isolated. It was identified by its chromatographic behavior on silica, mass spectrum, UV, and fluorescence spectra.

4- and More Rings. Azapyrenes, azafluoranthene, and traces of 11H-indeno(1,2-b)quinoline are the only 4-ring aza-arenes found in our samples. No benzacridine or diben-

zacridine was found, even though our detection limit for these compounds in the HPLC reversed phase is ≈ 1 ng.

It is interesting to note that we found much higher concentrations of 2-ring aza-arenes and progressively smaller amounts of higher ring compounds in our samples. The reverse observation was reported for the Antwerp sample studied by

Table I. Concentration of Aza-Arenes in New York City Suspended Particulate Matter

No.	Aza-arenes	Name	Mol wt	Concn in ng/1000 m ³	
				Sample 1	Sample 2
1		Quinoline	129	69	22
1a		Methylquinolines	143	35	33
1b		Dimethylquinolines	157	48	44
1c		Ethylquinolines	157	14	22
1d		3C-quinolines	171	10	ND ^a
2		Isoquinoline	129	180	140
2a		5 or 8 methylisoquinoline	143	310	170
2b		Other methylisoquinolines	143	76	70
2c		Dimethylisoquinolines	157	62	ND
2d		Ethylisoquinolines	157	160	68
2e		3C-isoquinolines	171	28	ND
3		Acridine	179	41	40
3a		Methylacridines	183	7	ND
4		Benzo(h)quinoline	179	10	13
5		Benzo(f)quinoline	179	11	10
6		Phenanthridine	179	22	18
7		Benzo(f)isoquinoline	179	110	34
8		4-Azafluorene (5-H-indeno[1,2-b]-pyridine) ^b	167	5	5
9		11H-indeno(1,2-b)quinoline	217	Trace	Trace
10		4-Azapyrene (benzo(1mn)-phenanthridine)	203	21 ^c	22 ^c
11		1-Azafluoranthene (indeno[1,2,3-ij]isoquinoline)	203	5 ^c	5 ^c
12		Benzothiazole	135	14	20
13		Caffeine	194	3400	7000

^aND: not determined. ^bName according to Patterson's Ring Index. All structures are also drawn according to the ring index. ^cIncludes other isomers.

Cautreels and Van Cauwenbergh (4). They found relatively higher concentrations of 4- and 5-ring aza-arenes compared to the 2-ring compounds. The fact that European cities generally burn more coal might explain this important difference.

Others. Benzothiazole, a common component in fuel oil, was found in Fraction 2. So far, no S-containing organic compound from particulate matter has ever been reported (19). The discovery of more S-containing compounds is expected to be found by using a sulfur selective flame photometric detector in GC.

Caffeine, in relatively high concentration, was found in Fractions 7 and 8. The ubiquity of coffee-roasting plants in New York City and in adjacent New Jersey might explain its presence. This finding is of biological interest since a recent assay has revealed that caffeine can inhibit the carcinogenic activity of polynuclear aromatic hydrocarbons (30).

This analytical study reveals valuable data on the composition of the basic fraction, both in terms of new compounds identified and their relative concentrations. The abundance and complexity of the quinoline and isoquinoline fractions, relative to other aza-arenes, should be noted. The recent findings on the carcinogenic properties of quinoline should be an additional reason for initiating more analytical work on the basic fraction. Nevertheless, since the observed quantities of aza-arenes are so minute and sufficient bioassays on these compounds are lacking, we hesitate to assign a biological significance to their presence in the basic fraction of urban pollutants.

Since the majority of the bicyclic compounds was probably lost during particulate matter collection by high-volume samplers, we are currently investigating trapping devices for quantitative sampling of semivolatile organics in the atmosphere. Improved sampling, coupled with a radioactive tracer for determining analytical recoveries, will definitely provide a more accurate and realistic assessment of the level of quinolines and other harmful volatiles in our cities.

Our approach should also be adaptable to other environmental sample types such as cigarette smoke, coal tar, and petroleum products where aza-arenes are present in relatively higher concentrations. Since aza-arenes, like polynuclear aromatic hydrocarbons, are pyrosynthesized during combustion, it is expected that they are widely distributed in the environment (31) and that they will receive more attention in future environmental research.

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Reversion of Histidine-Dependent Mutant Strains of *Salmonella Typhimurium* by Mississippi River Water Samples

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■ Fifty-three unconcentrated samples of Mississippi River water, collected at six different sites over a nine-month period, were examined with histidine-dependent mutant strains of *Salmonella typhimurium* for the presence of mutagens and potential carcinogens. Twenty-seven samples (51%) induced reversion to histidine independence with one or more of the mutant strains. Fifteen of the 27 samples (56%) first required metabolic activation before reversion was observed. Maximum numbers of samples producing reversion were collected during the late summer and autumn months. A correlation between increased river flow and the reduction in the number of samples producing genetic changes was noted.

The lower Mississippi River in southeastern Louisiana serves as the source of water for 40 water utilities which provide potable water for approximately 1.5 million people (1). In addition, Mississippi River water is introduced into Bayou Lafourche at Donaldsonville, where it is the source of raw water for four water treatment plants located along its banks.

Industrial wastes also are introduced into the Mississippi along the 256 river miles from St. Francisville to Venice, La., by at least 60 major industries including petroleum refineries and numerous diverse petrochemical and chemical manufacturers situated on the river banks. Most use the Mississippi as a process and/or cooling water source. All discharge either partially treated or untreated industrial wastes into the river (1).

Studies into the industrial pollution of the lower Mississippi River conducted by the U.S. Environmental Protection Agency have shown a broad spectrum of heavy metals, inorganic, and organic compounds to be present in concentrates of river water as well as in those of finished water obtained from water treatment plants utilizing the Mississippi as the source of raw water (1). Furthermore, at least three of the organic compounds identified in finished waters were considered to be either carcinogenic or potentially carcinogenic (1).

Although a variety of compounds have been detected in the concentrated extracts from finished waters, there is speculation as to whether these substances were present in sufficient concentrations to constitute a public health hazard when such waters were consumed. A recent report suggested that the presence of certain organic compounds detected in the sera of individuals living in the New Orleans area may have been due to the consumption of finished water originating from the Mississippi (2).

Our investigations have been concerned with the assessment of unconcentrated Mississippi River and finished water samples for the presence of mutagens, carcinogens, and/or potential carcinogens as evidenced by genetic alterations in appropriate testing systems exposed to the waters in question. In our studies, we have employed a bacterial system developed for the study of carcinogens (3). In our opinion, genetic changes induced by unconcentrated water samples provide an indicator of a potential public health hazard superior to that based upon chemical analyses of concentrated extracts.

The detection of mutagenic, carcinogenic, and/or potential carcinogens through the reversion of histidine-dependent mutant strains of *Salmonella typhimurium* has been reported (3-5). Preliminary investigations with a series of known carcinogens and potential carcinogens (i.e., those requiring metabolic activation) and the mutant tester strains duplicated the findings in the studies mentioned above, confirming our proficiency with this testing system. This report will present the findings obtained when various Mississippi River water samples were assayed with the bacterial strains described above.

Materials and Methods

Mississippi River Water Samples. Water samples were obtained near raw water intakes of six water treatment plants located approximately 50 river miles apart between St. Francisville and Pointe a la Hache, La., a distance of 220 river miles. Monthly collections were made by the Division of Water Pollution and Control (Louisiana State Department of Wildlife and Fisheries) staff. Water samples were collected in a brass "sampler" at a depth of 1-2 ft and immediately transported to the laboratory in wet ice.

Each sample was serially filtered utilizing positive nitrogen gas pressure. Water was first passed through a glass prefilter pad together with a Millipore membrane filter having an average pore diameter (APD) of 1200 nm, a 450-nm APD membrane, and finally through a sterile 200-nm APD membrane. Sterile filtrates were stored frozen at -20 °C.

Bacterial Tester Strains. Histidine-dependent mutant strains (TA 1535, TA 1536, TA 1537, and TA 1538) of *S. typhimurium*, recommended for the study of mutagenic and/or carcinogenic compounds, were employed in this investigation (5). Stocks of the strains were prepared and stored frozen at -90 °C in accordance with the instructions received. Strains TA 98 and TA 100 were employed later in other phases of this investigation.

Assay of Water Samples. Scrapings from the frozen bacterial stocks were employed as inocula for 20-mL volumes of nutrient broth containing 0.5% NaCl. The inoculated media were incubated at 37 °C overnight, then centrifuged at 250 × G for 20 min. The resulting pellet was resuspended in 2.5 mL of sterile 0.85% NaCl. This procedure has consistently resulted in concentrations of 1-2 × 10⁹ organisms/mL. Both the direct and the liver microsome-activated testing methods were employed in this investigation (4, 5).

Direct Testing Procedure. This consisted of inoculating 2 mL of a sterile water sample with 0.1 mL of the bacterial suspension described above. The mixture was then mixed with an equal volume of overlay containing 1.4% agar and poured over the surface of the agar base layer (4). Cultures were incubated, inverted at 37 °C for three days, and the resulting colonies counted.

Liver Microsome-Activated Testing Method. Attempts were made to activate metabolically potential carcinogens possibly present in the river water samples by adapting the liver enzyme-activation technique (5). The S-9 mixture was modified by the utilization of 0.45 mL of the S-9 fraction and 0.55 mL of the ingredient mixture. The S-9 fraction was modified in the following manner: Frozen guinea pig livers

were obtained from a commercial source (Pel-Freeze Biologicals, Inc., Rogers, Ark.), thawed, and washed with sterile normal saline. Washed livers were homogenized in 0.15 M KCl, with 3.0 mL of KCl solution for each gram of liver employed. The homogenate was centrifuged again at $17\,500 \times G$ for 10 min. The supernates from this centrifugation were pooled, placed in sterile vials, and stored at -90°C . The ingredient mixture was prepared in the manner described (5). The agar base layer and overlay were identical to that employed with the direct testing method.

The test consisted of combining 2 mL of sterile water sample with 0.1-mL suspension of a tester strain and 0.5 mL of the S-9 mix. The mixture was incubated at 37°C for 20 min, then added to 2.0 mL of overlay, and poured. Cultures were incubated as described in the direct testing method.

Controls. An integral part of each assay conducted included determining the normal reversion rates of each of the tester strains employed. The procedures used were identical to those described with the direct and liver enzyme-activation testing methods, except that distilled deionized water, sterilized by autoclaving, was used in lieu of aliquots of river water samples.

To ensure proper functioning of the test systems, diluted concentrations of known carcinogens, one capable of reverting the strains by direct exposure and the second requiring metabolic activation, were included with the respective tests. In the direct test, negative controls confirmed the sterility of the agar base layer, the overlay agar, the distilled-demineralized water employed in ascertaining the normal reversion rates of the strains, and the normal saline solution used to prepare the tester strain suspensions. When liver enzyme activation procedures were utilized, negative controls determined the sterility of the ingredient mixture, the liver microsomal fraction, and the S-9 mixture, in addition to those controls listed for the direct test method.

Evaluation of Testing Systems. Each water sample was screened initially by assaying the sample in triplicate in the direct testing method and in duplicate with the liver microsome-activated testing system. An equivalent number of positive and negative controls was included in both of the testing systems. Since polluting mutagens, or potential carcinogens, would be subjected to extreme dilution by the waters of the Mississippi, it was anticipated that the incidence of genetic reversion to histidine independence by the tester strains, if any, would be minimal. Accordingly, in both systems, if the average revertant colony count of the tested water sample were five or greater when compared with that of the control, the water sample was suspect. The suspect water sample was tested again, utilizing 10 culture plates each for

the water sample as well as for the appropriate controls. The reverted colony counts obtained were then subjected to statistical analyses. The standard deviation and variance for each sample were determined. The unpaired "T" test was utilized to determine probability. A probability of 0.05 or less was considered as significant.

It has been our hypothesis that the small concentrations of mutagenic and/or carcinogenic substances which have been reported to be present in waters of the Mississippi River will induce limited rates of reversion among tester strains exposed to such waters. Because of the very nature of the material being examined, it was anticipated that the reversion rates which would be obtained would be less than those considered to be significant by Ames et al. (4). Under such circumstances the significance of such changes could only be ascertained by means of statistical analyses.

To substantiate our methods, efforts were made to obtain dose-response data from Mississippi River water samples. Immediately following their collection, river water samples were clarified and sterilized by the methods previously described. Twofold serial dilutions of the samples were prepared with deionized, activated carbon-filtered distilled water which was sterilized by autoclaving. Each water sample and its respective dilutions were assayed simultaneously by the direct and liver enzyme-activated test procedures, with strains TA 1535, TA 1537, TA 1538, TA 98, and TA 100. Assays with each strain were carried out employing 10 replicate agar plates. Dose-response curves were prepared on those strains which showed an increased number of revertant colonies when exposed to the undiluted water sample.

Results

Samples of Mississippi River water collected at six different sites were examined with four tester strains of *S. typhimurium* (TA 1535, TA 1536, TA 1537, and TA 1538), utilizing both the direct and liver microsome-activated testing systems. Statistically significant rates of reversion to histidine independence were observed with three of the four tester strains. Strain TA 1536 was not reverted by any of the 53 river water samples when assayed with either of the testing methods.

Table I presents the statistical values obtained when the different water samples were assayed with strain TA 1535. Eleven river water samples (21%) induced reversion of this strain. Of these, seven (64%) were observed to induce significant reversion rates with the direct testing method only. Four samples (36%) required liver enzyme activation before causing significant rates of reversion. One sample (St. Francisville, 10/4/74) produced reversion with both testing methods.

In contrast to the findings noted with strain TA 1535, re-

Table I. Mississippi River Water Samples Producing Statistically Significant Reversion Rates with Mutant Strain TA 1535

Sampling site	Collection date	Testing systems	
		Direct	Liver-activated
St. Francisville	10/04/74	72.9/51.5 ^a ($p < 0.0005$; SD = ± 9.53)	25.4/15.7 ($p < 0.005$; SD = ± 7.76)
Plaquemine	2/12/75	28.4/23.5 ($p < 0.005$; SD = ± 2.547)	
Lutcher	10/04/74	63.2/51.5 ($p < 0.005$; SD = ± 11.18)	
Luling	9/11/74		27.1/15.7 ($p < 0.005$; SD = ± 10.5)
	10/04/74		26.3/15.7 ($p < 0.005$; SD = ± 7.42)
Belle Chasse	10/01/74		27.2/15.7 ($p < 0.005$; SD = ± 8.31)
	11/12/74	42.7/32.4 ($p < 0.005$; SD = ± 7.562)	
	12/10/74	43.5/32.4 ($p < 0.005$; SD = ± 8.10)	
Pointe a la Hache	10/01/74	66.1/51.5 ($p < 0.005$; SD = ± 10.28)	
	12/10/74	39.8/32.4 ($p < 0.005$; SD = ± 6.40)	
	10/01/74		26.8/15.7 ($p < 0.005$; SD = ± 7.25)

^a Mean reversion rate with water sample/mean normal reversion rate.

version of strain TA 1537 (Table II) was limited primarily to a series of river water samples collected during the middle of September. Of even greater interest is the observation that four of the six samples (67%) collected at this time required liver enzyme activation before causing this strain to revert.

Of the four tester strains recommended for use, strain TA 1538 was reported to be the most sensitive to reversion (5). This was confirmed in our observations with the Mississippi

River water samples (Table III). Twenty-one water samples (40%) were found to produce significant rates of reversion with this strain. Twelve samples (23%) caused reversion of this strain when tested directly. Nine of 21 samples (43%) causing reversion produced significant reversion rates only after metabolic activation with liver enzymes. Six samples produced significant reversions with both test systems.

Table IV summarizes the findings with river samples col-

Table II. Mississippi River Water Samples Producing Statistically Significant Reversion Rates with Mutant Strain TA 1537

Sampling site	Collection date	Testing systems	
		Direct	Liver-activated
St. Francisville	9/13/74		34.0/25.8 ^a ($p < 0.025$; SD = ± 9.42)
Plaquemine	9/13/74	14.1/10.9 ($p < 0.05$; SD = ± 3.51)	
Luling	9/11/74		33.3/25.8 ($p < 0.025$; SD = ± 8.83)
Belle Chasse	9/11/74		32.6/25.8 ($p < 0.005$; SD = ± 4.88)
Pointe a la Hache	9/11/74		32.6/25.8 ($p < 0.005$; SD = ± 5.146)
	4/14/75	8.5/6.3 ($p < 0.010$; SD = ± 2.173)	

^a Mean reversion rate with water sample/mean normal reversion rate.

Table III. Mississippi River Water Samples Producing Statistically Significant Reversion Rates with Mutant Strain TA 1538

Sampling site	Collection date	Testing systems	
		Direct	Liver-activated
St. Francisville	8/16/74	19.6/9.1 ^a ($p < 0.005$; SD = ± 6.14)	
	9/13/74	40.6/33.9 ($p < 0.005$; SD = ± 5.34)	
	10/16/74	24.9/20.3 ($p < 0.025$; SD = ± 4.43)	
Plaquemine	8/16/74	15.7/10.6 ($p < 0.005$; SD = ± 3.33)	41.4/33.9 ($p < 0.005$; SD = ± 6.915)
	9/13/74		33.3/29.6 ($p < 0.025$; SD = ± 3.05)
	10/31/74	15.0/11.4 ($p < 0.05$; SD = ± 4.853)	21.8/16.0 ($p < 0.010$; SD = ± 3.583)
	12/10/74		38.8/32.4 ($p < 0.005$; SD = ± 5.32)
Lutcher	8/16/74	15.3/10.6 ($p < 0.005$; SD = ± 4.09)	40.6/29.6 ($p < 0.0005$; SD = ± 4.57)
	19/13/74		37.9/29.6 ($p < 0.0005$; SD = ± 4.677)
	10/04/74		26.3/15.7 ($p < 0.005$; SD = ± 7.42)
	10/31/74		20.1/16.0 ($p < 0.05$; SD = ± 4.508)
Luling	8/16/74	15.2/9.1 ($p < 0.0005$; SD = ± 3.85)	36.4/29.6 ($p < 0.005$; SD = ± 5.481)
	9/11/74	47.3/33.9 ($p < 0.0005$; SD = ± 7.47)	
	10/11/74	27.7/20.3 ($p < 0.05$; SD = ± 6.53)	36.1/29.6 ($p < 0.005$; SD = ± 5.384)
	11/12/74		21.7/16.0 ($p < 0.025$; SD = ± 4.347)
Belle Chasse	8/10/74	19.6/9.5 ($p < 0.0005$; SD = ± 4.97)	36.3/21.6 ($p < 0.005$; SD = ± 10.53)
	9/11/74	14.5/10.6 ($p < 0.025$; SD = ± 4.79)	
	10/01/74		37.5/29.6 ($p < 0.0005$; SD = ± 3.894)
	4/14/75		27.6/20.0 ($p < 0.005$; SD = ± 4.903)
Pointe a la Hache	8/16/74	15.6/10.6 ($p < 0.005$; SD = ± 4.29)	
	4/14/75		28.1/20.0 ($p < 0.005$; SD = ± 5.259)

^a Mean reversion rate with water sample/mean normal reversion rate.

Table IV. Summary of Mississippi River Water Samples Tested and Specific Histidine-Dependent Mutant Strains of *Salmonella Typhimurium* Reverted by Such Samples

Sampling dates	River water sampling sites					
	St. Francisville	Plaquemine	Lutcher	Luling	Belle Chasse	Pointe a la Hache
8/16/74	4 ^a	4, 4a ^b	4, 4a	4, 4a	4, 4a	4
9/11,13/74	3a, 4	3, 4a	1a, 4a	1a, 3a, 4	3a, 4	3a
10/1,4/74	1, 1a, 4	1	1a, 4a	1a, 4, 4a	1, 4a	1a
10/31,11/12/74	...	4, 4a	4a	1
12/10/74	...	4a	...	1, 4a	1	...
1/06,14/75
2/04,12/75	1
3/06/75
4/06,14/75	NC ^c	4a	3, 4a

^a Tester strains showing significant reversion rates; 1 = TA 1535, 3 = TA 1537, 4 = TA 1538. ^b a = Significant reversion with indicated tester strain following exposure of water sample to liver microsome fractions. ^c NC = not collected.

lected sequentially at sampling sites from St. Francisville to Pointe a la Hache, La., during a 9-month period from August 1974 through April 1975. Twenty-seven of 53 river water samples tested (51%) produced significant reversion rates with one or more of the four tester strains. It may be noted that the waters collected at St. Francisville during the months of August–October already contained factors capable of producing significant reversion rates with the two testing systems employed. As shown in Table III, strain TA 1538 was most frequently reverted by the samples collected during the months of August–December. Water samples collected at the various sites during August only reverted strain TA 1538. In September the composition of the waters apparently became altered so that strain TA 1537, as well as strain TA 1538, was reverted. The composition of the water samples changed again in October, when reversions of strains TA 1535 and TA 1538 were observed. A seasonal variation in the composition of the water became apparent with the onset of the winter and early spring seasons, when scarcely any evidence of reversion showed with samples collected during this period. Of the 23 water samples collected during January–April 1975, only three (13%) induced reversion with one or more of the four tester strains using both testing methods.

The height of the Mississippi River at New Orleans on the dates of sample collection is presented in Table V. An inverse relationship appears to exist between the reduction in the number of samples inducing reversion among the tester strains during the winter and early spring samplings (Table IV) when compared with the river heights on the sampling dates.

Figure 1 illustrates the dose-response data obtained when two different samples of Mississippi River water were assayed in the manner described. Increased rates of reversion were observed when strains TA 98 and TA 100 were directly exposed to undiluted river water samples. A decrease in the number of revertant colonies was observed as dilutions of the respective samples increased.

Discussion

It has been estimated that a large proportion of human cancers are directly associated with environmental agents. While no association has yet been made between biological environmental agents and cancer in man, such an association has been proved for certain chemical and physical agents (6). In addition, recent concern has been expressed over the incidence of cancer and the chronic exposure of the general population to minimal concentrations of pollutants, mainly chemical, now present in the environment (7).

Specific conclusions cannot be drawn as to the types of the substances producing the reversion of strains summarized in Table IV. Because of the bacterial nature of the assay systems, the genetic changes observed must be considered as mutations. However, in those instances where significant rates of reversion were observed following liver enzyme-activation procedures only, it has been concluded by others that compounds which induce genetic changes only after metabolic activation must be considered as potential carcinogens (4).

The sensitivity of the different tester strains to reversion by the various water samples is consistent with the findings previously reported (5). Strain TA 1538 was observed to be the most sensitive, with no reversions being induced with any of the water samples assayed by either of the testing methods.

It is interesting to note that liver enzyme activity in six instances apparently altered the compounds in question, resulting in a loss of their mutagenic activity. These appear to be examples of mutagenic compounds becoming metabolized predominately to nonmutagenic forms (8). This was observed with 13 (25%) of the 53 water samples assayed, further

Table V. Mississippi River Heights at New Orleans, La., on Indicated Water Sampling Dates

Sampling date	Mississippi River ht at New Orleans, ft ^a
8/16/74	+3.4
9/11,13/74	+5.6, +5.6
10/01,04/74	+4.4, +4.4
10/31, 11/12/74	+3.1, +3.9
12/10/74	+5.7
1/06,14/75	+7.3, +10.3
2/04,12/75	+10.2, +12.5
3/06/75	+12.9
4/06,14/75	+16.6, +17.8

^a 0.0 Ft = mean sea level.

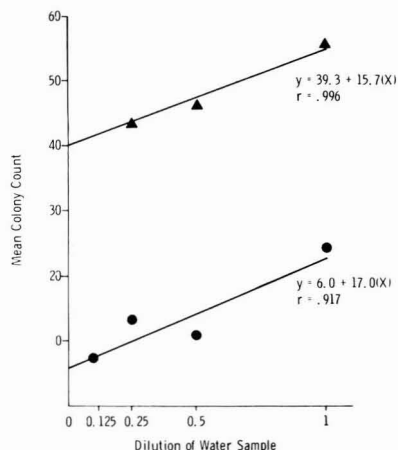


Figure 1. Dose-response data with Mississippi River water samples
 ▲ Sample collected, New Orleans, La., 12-11-76, vs. strain TA 100. ● Sample collected at Luling, La., 1-10-77, vs. strain TA 98

stressing the need of utilizing both testing systems when assaying water samples routinely.

Although the term "substance" is employed, on the basis of available data it does not imply that reversions may not have been induced by more than a single compound acting in unison. In some instances, mutations may have been induced as the result of synergism between two or more compounds with individual concentrations possibly too low to induce reversion alone. This phenomenon has been reported in investigations of cell transformation by smog condensates (9).

The majority of the samples inducing reversion with strain TA 1538 (Table III) appear to be clustered at the collection sites of Plaquemine, Litcher, and Luling (Figure 1). Granted a relationship cannot be reported at this time, the riverfront area, from Baton Rouge to Luling, also is the site of some 42 petroleum and chemical plants.

Although the results summarized in Table IV indicate a monthly qualitative variation in the composition of the water samples, it is not possible to elaborate further on this aspect at this time. However, during the warmer months (i.e., August–October 1974) compounds inducing reversion appear to have been introduced into the Mississippi River at some location above St. Francisville. With the onset of colder weather, the reversions observed appear to be induced by local influences.

Two considerations may explain the apparent lack of activity with samples collected during the winter and early

spring months. First, colder water temperatures may reduce the biological activity in the river waters which could metabolize a variety of compounds into a more active form. A second, and perhaps more realistic explanation, is that of simple dilution. Even if mutagenic compounds are introduced into the river waters in constant quantities, their concentrations could be reduced to undetectable levels with an increase in the river flow from thawing of winter snows and seasonal increase in precipitation in the areas drained by the river.

Maximum height of the river at New Orleans was 17.8 ft, cresting in mid-April with a gradual decline recorded subsequently. We expect that water samples will again produce reversions with the tester strains when the river waters recede to lower levels.

For this investigation, only unconcentrated water samples were examined. Our data reasonably infer that those compounds present in the water samples, capable of producing genetic alteration among the bacterial tester strains employed, also may be present in sufficient quantities to induce carcinogenesis through somatic mutation when such waters are consumed.

Presently, conclusions cannot be deduced, but our findings do suggest that a potential threat to consumers of finished waters of river origin during the late summer and autumn months does exist and that this threat subsides as river flow increases. More extensive qualitative and quantitative investigations are necessary to determine definite conclusions or solutions.

Analytical studies have indicated that mutagenic substances in unconcentrated water samples would be present in minimal quantities. As mentioned previously, we anticipated that those tester strains exposed to such minimal concentrations would show minimal reversion rates. Because of this, statistical analyses were employed to detect significant differences.

Although our methodology deviated somewhat from that previously reported (4, 5), we consider it valid since we have shown increases in the number of colonies reverted with increasing concentrations of substances in a given water sample.

Our findings indicate that the individual sensitivities of the tester strains to the mutagens encountered were in complete agreement with those reported (5). Furthermore, there were numerous instances where significant reversion rates were observed only after exposure of the water samples to liver microsomal fractions. In addition to those reported here, a variety of other water samples were assayed with the tester strains. Strain TA 1536, described as being the least sensitive

to reversion, was not reverted by a single water sample tested.

If the values obtained were due to factors other than to mutagenic effect by substances present in the water samples, the reversions we observed should have appeared at more random among the strains. It is also difficult to explain why such factors often appeared following liver activation only. The selective nature of these factors affecting only three of the four tester strains cannot be explained by mere chance. It can only be concluded that the reversions observed were real and were due to substances present in the water samples assayed.

Acknowledgment

We thank L. R. Kuss and the staff of the Division of Water Pollution Control, Louisiana State Department of Wild Life and Fisheries, for their cooperation in this investigation; T. L. Bradley and W. C. Dixon for their invaluable assistance in providing the water samples; and G. F. Craun, project officer, for his administrative assistance.

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NOTES

Preparation of Stained Alginate Beads for Photosensitized Oxidation of Organic Pollutants

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Present procedures for reducing the content of organic pollutants in industrial effluents fall generally into two broad categories, those involving the application of some chemical substance which reacts with the pollutant, and biodegradation. The former generally require a relatively large input of energy, as with chlorine or ozone, or as with adsorption on activated charcoal, for preparation and regeneration of the

absorbent. Biodegradation may require much time, and if the pollutant is very toxic, either high dilution or special cultures.

Some organic pollutants, including very toxic ones, are susceptible to what may be regarded as a third treatment process, photosensitized oxidation (1). In this process a photochemical catalyst or sensitizer enables the energy of sunlight

■ Gelled beads of alginate were prepared and stained with various dyes for the heterogeneous phase sensitization of the photooxidation of organic compounds in water. When oxidation of phenols is intended, the beads may be prepared with

basic salts within them to ionize the phenol. A number of phenols were oxidized in aqueous solution with these beads; the oxidations of *p*-cresol and pentachlorophenol are illustrated.

to effect oxidation of the substrate pollutant by atmospheric oxygen. Classes of pollutants susceptible to this process include amines, olefins, mercaptans, and phenols. Immediate application of this process is hindered by the instability of many active photosensitizing dyes in water and the need to separate the treated water from the dye and its photolysis products. Both of these obstacles could be largely overcome by performing the treatment in a suitable heterogeneous phase system. We report here the preparation of a material which may be the basis of such a treatment process, consisting of gelled beads of the natural polysaccharide, alginic acid, stained with photosensitizing cationic dyes.

We have tested this material on a laboratory scale with aqueous solutions of phenols. These were chosen as substrates because they are present in large quantity in industrial effluents (2), in particular from refineries and coal processing, and because their extreme toxicity to fish, and taste and odor problems require that they be essentially eliminated from productive fresh waters (3) and from municipal water supplies (4).

The mechanisms of photosensitized oxidation and its application to organic compounds have been reviewed by Gollnick (5), and the oxidation of some phenols has been studied by Weil et al. (6). This process, which requires visible radiation, should be distinguished from the direct photolysis of phenols, which requires ultraviolet radiation (7). Photooxidation of phenols sensitized by ZnO and other minerals in near ultraviolet radiation has been investigated with some success (8).

Preparative Procedures

Materials. Several samples of commercial grade Na alginate have been used, including gifts from the Kelco Chemical Co. and Alginate Industries Ltd., and all served equally well. The alginate solutions had usually been dialyzed to remove salts in connection with other work, but this was not necessary.

A variety of dyes have been used, including phenosafranine, acridine orange, acriflavin, crystal violet, pararosaniline, methylene blue, thionine, and toluidine blue, with varying degrees of success, but the last three thiazine dyes were most active. The phenols and other reagents were commercial materials, used as received.

Preparation of Beads. Beads were prepared by adding a solution of Na alginate dropwise to a gently stirred solution of a salt of Ca^{2+} , Sr^{2+} , or Ba^{2+} . Alginate solutions in the range of $1.5\text{--}8.3\text{ g L}^{-1}$ were used. The salt solution should be at least 10^{-3} M ; $3 \times 10^{-2}\text{ M Ba(NO}_3)_2$, 10^{-1} M CaCl_2 , and $10^{-1}\text{ M Sr(OOCCH}_3)_2$ are typical of the concentrations employed.

As soon as a drop of alginate enters the salt solution, an invisible pellicle surrounds it, protecting it from dissolution or merging with other drops. As the salt solution continues to penetrate the drop, it contracts and becomes gelled throughout. The drop gradually sinks as it shrinks to about $\frac{1}{4}\text{--}\frac{1}{3}$ of its original volume, and becomes easily visible by scattered light. Beads typically about 4 mm diameter were thus formed, which tend to shrink gradually with repeated use.

The beads are weakly elastic, have a jelly- to putty-like consistency, and are easily cut. They do not adhere to each other or to surfaces, but cohere sufficiently to resist abrasion

by mild mechanical stirring. In water or dilute salt solutions they retain consistency, size, and shape indefinitely (>2 years). Out of water, they slowly shrink by syneresis into barely visible flakes. They are subject to chemical dissolution by acids, strong alkali metal salt solutions, and strong complexing agents for the crosslinking alkaline earth metal ions.

Attempts to prepare beads of Al^{3+} alginate by this method produced only a mush. Al alginate beads could be formed by treating preformed Ca alginate beads with a solution of alum. Incorporation of Al^{3+} into the beads is evidenced by the capacity of the beads for staining with alizarin and other chelating agents for Al^{3+} (9).

Staining of Beads. When the beads were completely gelled and had stabilized in size, they were separated from the solution of preparation by draining through a Buchner funnel. They were then washed by equilibration with several changes of water to remove excess salt, and covered with a ca. $1 \times 10^{-3}\text{ M}$ solution of the dye. Initial uptake of dye was complete in a few minutes, but 24 h standing allows the dye to become more evenly distributed within the beads. The ratio of equivalents of alginate carboxylate groups to dye ranged from 30 to 200.

Filled Beads. The stained beads are fully capable of sensitizing oxidation of organic substrates in sunlight or artificial light. However, if phenols are to be treated, as in the present case, it is necessary to establish alkaline conditions (6, 10). Base may be added to the water to be treated, in sufficient quantity to ionize the phenol and neutralize the acids formed during oxidation. Although addition of base (e.g., Na_2CO_3) to the water was effective, it was considered more advantageous to establish alkaline conditions within the beads themselves, by incorporating slightly soluble basic minerals such as CaCO_3 , SrCO_3 , BaCO_3 , MgCO_3 , or dolomite [approximately $\text{Ca}_2\text{Mg(CO}_3)_2$]. The mineral is mixed into the alginate solution before the beads are formed.

Dissolution and hydrolysis of the filler salt establish a mildly basic environment within the bead and a pH gradient across the surface into the bead. Phenols in the surrounding water diffuse up the gradient to become ionized within the bead and are then destroyed in the light. In this way, phenols can be eliminated without the water becoming very basic at all.

Filled beads are noticeably less retentive of dye than unfilled, because of competition with the metal of the filler. However, they retain enough dye to be effective and can easily be recovered and restained after a reaction.

Apparatus. The ability of stained beads to destroy phenols in water was demonstrated in an apparatus consisting of a three-necked flask, irradiated by a 750-W projector lamp at a distance of 22 cm. The radiant intensity behind the flask was about $1.25 \times 10^5\text{ erg cm}^{-2}\text{ s}^{-1}$, as measured with a Kettering radiant power meter. Volumes of about 800 mL of phenol solution were treated at a time. The beads were kept in motion by magnetic stirring, and a slow stream of O_2 was passed into the solution to maintain near saturation. The flask was placed in a bath cooled by running tap water, which held the temperature to $18\text{--}20^\circ$.

At intervals of an hour or more, spectra of samples were recorded on a Cary 14 spectrophotometer. The destruction of phenols was followed by the alteration of the spectrum, as the characteristic bands of the phenol were replaced by the

broader bands of oxidized products (10). During some reactions the fall in COD of the solution was monitored with a Precision AquaRator.

Oxidation of Phenols

A number of phenols have been successfully treated, but two examples will suffice to illustrate the photosensitizing activity of the beads. The oxidation of the more easily oxidized phenols, such as guaiacol, often produces large amounts of strongly colored materials, sometimes loosely termed "melanins". Oxidation of *p*-cresol in the presence of the relatively mild base dolomite (Figure 1) resulted in very slight discoloration of the water. The absorption band of cresol at 275 nm was replaced by steadily rising absorption into the ultraviolet, with little extension into the visible, at a rate estimated from the spectral change as about 6%/h.

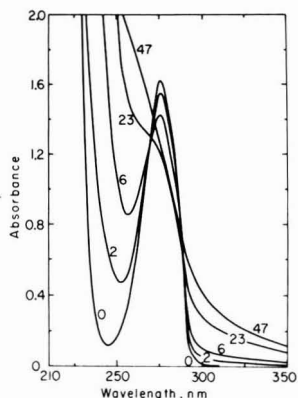


Figure 1. Oxidation of *p*-cresol (1.015×10^{-3} M) photosensitized by toluidine blue on Ca alginate beads containing dolomite. Beads were prepared by adding 25 mL of 0.83% Na alginate solution mixed with 0.9 g dolomite to 150 mL of 0.1 M CaCl_2 solution and stained with 5×10^{-6} mol of toluidine blue. Spectra recorded on samples diluted 1:1 with 0.1 M HCl in 1-cm path length cell after 0, 2, 6, 23, and 47 h of irradiation. Spectra taken before acidification were similar.

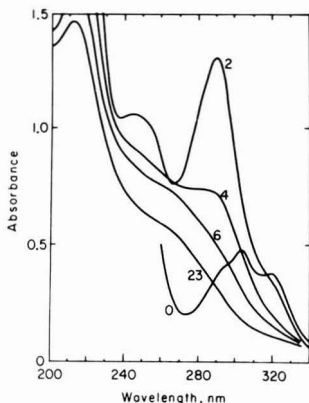


Figure 2. Oxidation of pentachlorophenol (1×10^{-4} M) photosensitized by toluidine blue on Sr alginate beads containing SrCO_3 . Beads were prepared by adding 25 mL of Na alginate solution, 7.5×10^{-3} N (0.15%), containing 0.73 g SrCO_3 , to 0.1 M $\text{Sr}(\text{OOCCH}_3)_2$ solution, and stained with 5×10^{-6} mol of dye. UV spectra recorded in 2-cm path length cell after 0, 2, 4, 6, and 23 h irradiation.

The destruction of a quite different sort of phenol is illustrated in Figure 2. Pentachlorophenol is a very stable material used for wood preservation, etc., which is degraded only by special cultures of bacteria (11), and which has been taking on the character of a general environmental poison (12). In 2 h the phenol appeared to be almost entirely replaced by a compound with an absorption band at 291 nm, which in turn was degraded in the course of a day to material with indistinct bands in the ultraviolet.

Much of the toxicity of phenols is presumed due to their aromatic character. We believe the aromatic character is largely lost through photosensitized oxidation, because the products do not appear to have the distinct bands in the 260–280-nm region associated with the phenyl group, and the COD in some cases (guaiacol, *p*-chlorophenol) was reduced to a value incompatible with the retention of a large fraction of unbroken phenyl rings.

Discussion

Much of the success of alginate as the support material is owing to its unique gelling properties with divalent metal ions. Our contribution to the literature of ion binding to alginate has been presented elsewhere (9, 13). Incorporation of the dye in porous beads of gelled alginate makes it possible to conduct sensitized oxidations in a heterogeneous phase system and to separate the treated water from the beads by draining. The beads were usually recovered after a reaction and could be retained when necessary and reused.

It is possible to consider large-scale application of this material to treatment of phenol-containing waters in industrial lagoons open to the sunlight. The intensity of sunlight is about five times the light intensity used in our apparatus; therefore, the extent of reaction achieved in 24 h of projector lamp light would be expected in 5 h of direct sunlight. Indeed, small-scale tests in direct sunlight indicate that this is so.

Alginate is a nontoxic, biodegradable carbohydrate and in fact is a bulk ingredient of food. The dyes used are not noted for either their stability or their toxicity, and in the quantities required are unlikely to introduce significant toxic residues into treated waters. The products of photooxidation of phenols are not known, and the degree of their toxicity would have to be evaluated were a large-scale application of this method contemplated.

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INDUSTRY TRENDS

IU Conversion Systems, Inc. will construct a multimillion-dollar facility to stabilize SO₂ scrubber waste products for the Petersburg Generating Station of Indianapolis Power & Light Co.

Envirotech Corp.'s Buell Division (Lebanon, Pa.) has won a \$3.3 million contract to provide 30 fabric filter units as part of the expansion of the P.T. Semen-Gresik (Persero) cement plant, East Java, Indonesia.

RETA/Nolte (St. Louis, Mo.) has received a design contract to upgrade the wastewater treatment plants for South San Francisco, Burlingame, Milbrae, and the San Francisco airport, in California. RETA is a division of Envirodyne Engineers

Resource Planning Associates (Cambridge, Mass.) has recently been awarded a Federal Power Commission contract to evaluate sites for liquefied natural gas terminals in the New England area. The

company specializes in scarce resource problems.

FMC Corp.'s Environmental Equipment Division has been awarded a contract in excess of \$8 million to design and install a flue gas desulfurization system for Southern Indiana Gas and Electric Co.

The Emanon Co., Inc., suppliers of instrument control panels for simulating testing on entire power and process systems, has moved to larger facilities in Canton, Mass.

Stanley Consultants, Inc. (Muscatine, Iowa) has done value engineering studies that will help the U.S. Army Corps of Engineers save \$4 million on the Lake Chicot, Ark., pumping plant, and prevent water pollution.

Nittetu Chemical Process Inc. has started business at Jenkintown, Pa.; among its services will be destruction of hard-to-treat or toxic effluents. The firm is owned by Nittetu Chemical Engineering Ltd. (Japan).

Combustion Engineering's C-E Power Systems announced that its five operating nuclear units posted a combined 83.5% reactor availability, the best 1976 performance in the U.S. nuclear industry.

The Ric-wil Co., Ltd. has opened a new sales office at Oakville, Ont., Canada. The firm, of Brecksville, Ohio, manufactures preinsulated, prefabricated piping systems for water, steam, oil, and other fluids.

Environmental Elements Corp. (Baltimore, Md.) has named O.P.G., Inc. (Pittsburgh, Pa.) as western Pennsylvania sales representative for the Scrubber/Filter Products Department.

Scientific Systems Services (Satellite Beach, Fla.) has received three contracts for more than \$250 000. One contract involves wind detection and monitoring.

Stone & Webster Engineering Corp. announced that the Nuclear Regulatory Commission has issued design approval for a third variation of the S&W standard plant. The design incorporates a 1200-MWe Westinghouse pressurized water reactor.

STRAAM, Water Resources Engineers, was formed at Portland, Oreg., to market the combined engineering services of two operating subsidiaries of CRS Design Associates, Inc.

The American Iron and Steel Institute (Washington, D.C.) said that domestic steel companies spent a record \$489 million for pollution control facilities in 1976, as compared to \$453 million in 1975.

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101



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This indicator/control station is a compact (3 X 6 in.) solid-state device that permits visual indication of a measured variable; for example, flow in gpm. Flashing digits show high/low alarm conditions. Set point adjustment can be manual or automatic. Applications in water/wastewater facility operation. General Signal

103

Alkalinity reagent

This reagent allows use of DS conductivity meters for measuring boiler water pH, typically 10-12. However, the reagent counteracts factors that cause erroneous pH readings at values of higher than 12. A chart is provided to ease conversion of obtained readings to pH. Myron L. Company

104

Flow monitor

This flow monitor utilizes the principle of sonar-in-air. It can therefore continuously measure the volume in gal of effluent flow, totalize the measurement, and record data on a chart recorder. Field calibration is made easy, and temperature is compensated for automatically. Environmental Measurement Systems

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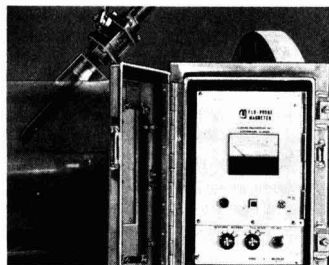
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Pit liner

Permanent, yet economical fiberglass reinforced plastic (FRP) liners can be used for salt water pits, chemical and fresh water storage plants, and sewage disposal plants. They will withstand years of sun, heat, ice, and corrosive fluids with no cracks, punctures, or seepage. They are transported to the job in pre-prepared rolls. Kote-Line, Inc.

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Flowmeter

Flowmeter will operate not only in freshwater pipes, but in debris-laden water and raw sewage and erosive sand slurries. Newly available teflon-titanium probe allows service in highly corrosive liquids. Familiar electromagnetic flowmeter has new configuration. Cushing Engineering

112

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New, all-PVC hose is added to line of vapor recovery hoses, and is specifically designed to return gasoline vapors to the tank truck during bulk gasoline delivery at service stations. Hose resists hydrocarbon vapors and abrasion. B.F. Goodrich

113

Instrument control valve

New instrument control valve is designed with a built-in positioner on an integral mounting bracket. Rubber sleeve is specially designed, reinforced with synthetic fiber cord. ISA specifications are met. Valve is part of Series 5200 H. Red Valve Co.

114

Ammonia/amine detection

New reagent, "Fluoropa," is the most sensitive addition to the small family of reagents suitable for detection of primary amines in chromatographic column effluents. Reagent can also detect peptides, proteins, amino sugars, polyamines, and ammonia. Pierce Chemical

115

GC detector

This gas chromatographic (GC) detector is halogen-specific. It is microcoulometric, and offers a sensitivity of more than 10^6 for chlorine over carbon, and 10^4 for chlorine over nitrogen, phosphorus, sulfur, and other interfering elements. Envirotech Corp.

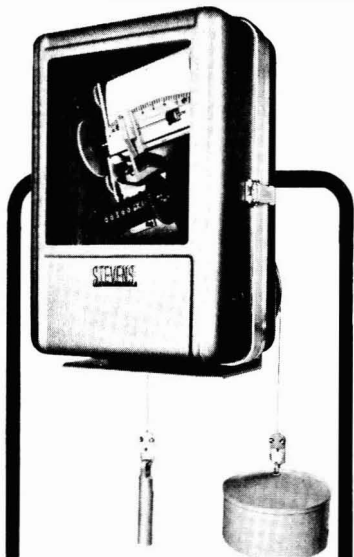
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Portable pollution meters

New series 300 pollution meters measure pollutants such as SO_2 , NO_x , H_2S , NO_2 , and CO. They are useful for stack monitoring and OSHA applications. Set-up and measurement takes only minutes. Sensor is stable, and less affected by temperature; it offers up to one year of use. System includes sample pump and conditioning unit, battery pack, and chargers. Ecology Board.

117

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Noise elimination for air. Bulletin PUL-1-111 describes the Compressor Pulse Trap, which eliminates noise and vibration in plant air compressor piping systems. American Air Filter Co., Inc. **151**

Corrosion-resistant pumps. Bulletin GP-2 describes fiberglass pumps. Waste treatment, power plants, mining operations, and petroleum are among the many applications. Fybroc, Inc. **152**

Aquatic sampling. Aquatic Sampling Supplies brochure tells about applications for water/waste sampling, well sampling, core sampling, biological specimen taking, and other uses. Horizon Ecology Co. **179**

Hazardous wastes. The January 1977 issue of *RESCUE* publishes exclusive interviews with Sen. Jennings Randolph (D, W.Va.), and Beatrice Tylutki of the New Jersey Dept. of Environmental Protection, concerning the Solid Waste Disposal Act (P.L. 94-580). Rollins Environmental Services, Inc. **180**

Corrosion-free pumping. New publication, "Vanton Flowliner," talks about corrosion-free plastic pumping equipment. Publication will be issued as a periodical newsletter. Vanton Pump and Equipment Corp. **181**

Wastewater instrumentation. Bulletin No. 150 discusses optimum instrumentation of equipment sold by company. Instruments are sold as adjuncts to process equipment, not separately. Industrial Waste Treatment Division, Ecodyne Corp. **182**

Air flow measurement. Indicator, described in Form 4071, allows visual monitoring of air flow through filter elements in spray paint booths to satisfy OSHA rules. Conco, Inc. **183**

Filter press. Catalog D-753 describes filter press units designed to dewater sludges efficiently. Solids recoveries exceed 98%; filtrate solids are as low as 0.1%. The Ralph B. Carter Co. **184**

Air pollution control. Bulletin B0401-7608 discusses wet and dry collection systems for air pollution control and process applications. Fans and blowers, and other equipment are listed. Entoleter, Inc. **185**

Filtration. Quarterly newsletter, *Filter Forum*, discusses difficult, yet common, filtration problems, and tells how a wide range of industrial companies have solved them. Balston, Inc. **186**

Safety supplies. March 1977 catalog lists over 1000 safety items to assist in meeting OSHA regulations. Interex Corp. **187**

Trommel screen. Specification Sheet No. 4080 tells of the usefulness of trommel screens to solid waste processing equipment; permits use of small shredder. Capacity 13.5–60 t. Koppers. **188**

Sewer cleaning. Catalog describes "Camel," an innovation in total sewer and catch basin cleaning. Cleans sewer hydraulically with 2000 psi of water, and has many other features. Super Products. **189**

Water analyzer. Brochure describes Model 1600 analyzer for total oxygen demand, total organic carbon, and total carbon in water. Curtin Matheson Scientific, Inc. **190**

Metal removal. Brochure U5M describes patented system for removing chromates and metals from cooling tower blowdown and other applications, such as metal finishing. No pH adjustment or chemical addition needed. Andco Inc. **191**

Sodium analyzer. Bulletin No. B-5-101 describes the Model 4000 pNa sodium analyzer as a selective-ion electrode analyzer/recorder. Measures sodium concentration in water. Calgon Corp. **196**

Clarifier. Clarifier Bulletin 129 describes Spirafloc clarifier that eliminates "short circuiting" problems associated with centerfeed clarifiers. Settled sludge can act as "filter" for fines. Lakeside Equipment Corp. **197**

Sampling control. Brochure describes the 104 Controller, which calculates water flow volume and automatically selects rate of sample flow. Fully solid state. Proportional-to-flow method gives more representative samples. Environmental Measurement Systems. **198**

Low temperature. Bulletin 114 describes low-temperature equipment (0 to -115 °F) for hydrocarbon vapor recovery, freeze drying, moisture removal, and other applications. Tenney Engineering, Inc. **199**

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BOOKS

Interim Performance Criteria for Solar Heating and Cooling Systems in Commercial Buildings, NBSIR 76-1187. National Technical Information Service, Springfield, Va. 22161. 1976. \$5.

These criteria are intended primarily for the solar demonstration program. They are aimed at providing a basis for more definitive performance criteria at a later date. However, they do have the objective of establishing technical performance levels of the commercial heating/cooling demonstration program, and for the procurement of systems, subsystems, and components for that group. The criteria, to be updated periodically by the National Bureau of Standards as more data become available, were developed with ERDA funding.

Stormwater Modeling. Donald E. Overton, Michael E. Meadows. xii + 358 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1976. \$22.50, hard cover.

Perhaps the biggest problem in water pollution abatement will be non-point sources, including stormwater. But before anything can be done about it, some idea of how stormwater travels, and what its fate is, must be known. This book presents predictive models of excess rainfall, open-channel flow, quality, and other related parameters.

Environment and the Industrial Society. Nicholas Homes, Ed. 247 pages. Westview Press, 1898 Flatiron Court, Boulder, Colo. 80301. 1977. \$15, hard cover.

The book analyzes the structure of industrial societies vis-à-vis the environmental crisis to identify potential routes to environmental stability—toward less consumption and better waste management practices. The several chapters deal with industrial and urban pollution, economics of pollution control, population growth, city design and transportation systems and resource depletion, among other topics.

Air Pollution Control and Design Handbook, Part I. Paul N. Cheremisinoff and Richard A. Young, Eds. x + 704 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1977. \$39.50, hard cover.

Air pollution was brought on by our technological wizardry and exacerbated by the twentieth-century lifestyle. But the problem is now being attacked with legal and economic dedication. This book was especially written for those managers faced with pollution problems from stationary sources; it offers analyses and recommendations of experts in several problem areas. The stress is always on

the practical aspects of pollution abatement.

Biological Responses of Marine Biota to Pollutants. F. John Vernberg et al., Eds. xiii + 462 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1977. \$21.50, hard cover.

With pollution of marine waters continuing, witness the rash of oil tanker accidents recently, this volume fulfills a valid need. Chapters cover the influence of petroleum products, pesticides, heavy metals and PCBs—acting alone or synergistically or interacting with normal environmental factors—on marine organisms.

Water and Wastewater Treatment: Calculations for Chemical and Physical Processes. Michael J. Humenick, Ed. 236 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1977. \$19.75, hard cover.

This book is devoted entirely to problem solving, with references accompanying each chapter. Topics covered include ion exchange, activated carbon

adsorption and coagulation, and flocculation.

Synthetic Fuels Processing. Arnold H. Pelofsky, Ed. xi + 473 pages. Marcel Dekker, Inc. 270 Madison Ave., New York, N.Y. 1977. \$35, hard cover.

The papers in this volume were presented at a 1976 symposium sponsored by the Division of Industrial and Engineering Chemistry of the American Chemical Society. Together these papers provide a fairly exhaustive analysis of the economics of several types of fuel processing.

Social, Economic and Environmental Implications in Transportation Planning. 95 pages. Transportation Research Board, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1977. \$4, paper.

This Transportation Research Record No. 583, comprised of nine reports, includes papers on "Issue-Oriented Approach to Environmental Impact Analysis," and "Incorporating Economic Considerations in the Preparation of Environmental Impact Statements."

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Write: Conference Office, Atomic Industrial Forum, Inc., 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

June 25 Minneapolis, Minn.

ASTM Symposium on Native Aquatic Bacteria, Enumeration, Activity and Ecology. American Society for Testing and Materials, Committee D-19 on Water

Write: Dr. R. R. Colwell, Dept. of Microbiology, Division of Agricultural and Life Sciences, University of Maryland, College Park, Md. 20742; or Dr. J. W. Costerton, Dept. of Biology, University of Calgary, 2920 24th Avenue N.W., Calgary, Alberta, Canada T2N 1N4

June 27 New York, N.Y.

The Outlook for Coal: Critical Times for a Critical Fuel. The Energy Bureau Inc.

Write: Robert W. Nash, executive director, The Energy Bureau Inc., 101 Park Ave., New York, N.Y. 10017

June 27-28 San Francisco, Calif.

Cooling Tower Institute Meeting. Cooling Tower Institute

Write: Dorothy Garrison, 9030 IH-45 N., No. 216, Houston, Tex. 77037

July 6-8 Moscow, Idaho

Energy, Environment and Wild Rivers in Water Resources Planning and Management. American Society of Civil Engineers, University of Idaho and Washington State University

Write: American Society of Civil Engineers, 345 E. 47th St., New York, N.Y. 10017

July 10-15 Rindge, N.H.

Non-Conventional Siting of Power Plants. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 10-15 Chicago, Ill.

Intersociety Conference on Transportation. IEEE, ASME, AIAA, AIIE, ASCE, EIC, ITE, SAE, SNAME and others

Write: Engineers Joint Council, 345 E. 47th St., New York, N.Y. 10017

July 13-15 Nashville, Tenn.

1977 ASCE National Conference on Environmental Engineering. American Society of Civil Engineers

Write: Edward L. Thackston, professor, Vanderbilt University, Environmental and Water Resources Engineering, Nashville, Tenn. 37235

July 17-22 Henniker, N.H.

An Assessment of Environmental Regulation. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 17-22 Rindge, N.H.

A Critique of the OSHA Program. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 24-27 Seattle, Wash.

Nuclear Power Financial Considerations. Atomic Industrial Forum, Inc.

Write: Atomic Industrial Forum, Inc., Conference Office, 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

July 24-29 Geneva, N.Y.

1977 Symposium for Innovation in Measurement Science. Instrument Society of America

Environmental topics will be discussed. *Write:* Peter Vestal, Instrument Society of America, 400 Stanwix St., Pittsburgh, Pa. 15222

July 31-August 5 Rindge, N.H.

Clean Combustion of Coal. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 1-6 Boulder, Colo.

Conference on Air Quality Meteorology and Atmospheric Ozone. American Society for Testing and Materials/Committee D-22 on Methods of Sampling and Analysis of Atmospheres

Write: Alvin L. Morris, president, Ambient Analysis, Inc., P.O. Box 4056, Boulder, Colo. 80306

August 3-5 Denver, Colo.

26th Annual Conference on Applications of X-Ray Analysis. University of Denver and Denver Research Institute

Write: Mrs. Mildred Cain, Denver Research Institute, University of Denver, Denver, Colo. 80208

August 8-9 Lewisburg, Pa.

9th Mid-Atlantic Industrial Waste Conference. Bucknell University

Write: Dr. Michael LaGrega, Civil Engineering Dept., Bucknell University, Lewisburg, Pa. 17837

August 10-12 College Station, Tex.

Coastal and Ocean Engineering; Environmental Engineering in the Coastal Zone. Texas A&M University and American Society of Civil Engineers/Brazos County Branch

Write: American Society of Civil Engineers, 345 E. 47th St., New York, N.Y. 10017

August 15-19 New Hampton, N.H.

Environmental Sciences: Air. Gordon Research Conferences

Write: Alexander M. Cruickshank, director, Gordon Research Conferences, Pastore Chemical Laboratory, University of Rhode Island, Kingston, R.I. 02881

(continued on page 634)

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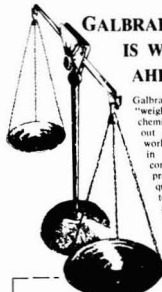
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June 27-30 Research Triangle Park, N.C.

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Fee: \$140. Write: Registrar, Air Pollution Training Institute, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

June 27-July 1 Cincinnati, Ohio
Effluent Monitoring Procedures: Flow Measurement and Sampling Techniques, Course No. 164.5. U.S. EPA

Fee: \$175. Write: Registrar, National Training and Operational Technology Center, MOTD, OWPO, WHM, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

July 5-15 Fort Collins, Colo.
Institute on River Mechanics—Modeling of Rivers. Colorado State University

Fee: \$600. Write: H. W. Shen, Engineering Research Center, Colorado State University, Fort Collins, Colo. 80523

July 11-13 Research Triangle Park, N.C.

Determination of Polycyclic Aromatic Hydrocarbons, Course No. 465. Air Pollution Training Institute

Fee: \$105. Write: Registrar, Air Pollution Training Institute, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

July 11-15 Cincinnati, Ohio
Effluent Monitoring Procedures: Basic Parameters for Municipal Wastewaters, Course No. 164.1. U.S. EPA

Fee: \$175. Write: Registrar, National Training and Operational Technology Center, MOTD, OWPO, WHM, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

International

June 20-24 Toronto, Ontario
70th APCA Annual Conference & Exhibition. Air Pollution Control Association

Write: Public Relations Dept., Air Pollution Control Association, P.O. Box 2861, Pittsburgh, Pa. 15230

July 4-15 Cambridge, England
NATO Study Institute on the Scientific Basis of Flocculation. NATO

Write: Prof. K. J. Ives, Course Director, Dept. of Civil & Municipal Engineering, University College London, Gower St., London WC1E 6BT England

July 18-22 Taipei, Taiwan
Pollution Control Equipment Exhibition. United States Dept. of Commerce

Write: Joseph Burke, project manager, Office of International Marketing, East Asia Group, Room 3016, U.S. Dept. of Commerce, Washington, D.C. 20230

July 18-21 Cambridge, England
INTER/MICRO-77. McCrone Research Institute

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July 23-August 19 St. Croix
Theory and Practice of Desalination. Fairleigh Dickinson University

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August 22-25 Bangkok, Thailand
International Conference on Computer Applications in Developing Countries. Asian Institute of Technology

Environmental topics will be discussed. Write: Dr. Fook Loy Ng, Secretary ICCA, Asian Institute of Technology, P.O. Box 2754, Bangkok, Thailand

August 22-26 Dunedin, New Zealand
International Symposium on Microbial Ecology

Write: The Executive Officer, The Royal Society of New Zealand, P.O. Box 12249, Wellington, New Zealand

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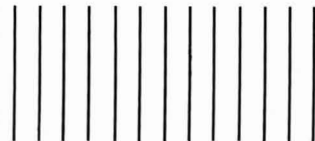
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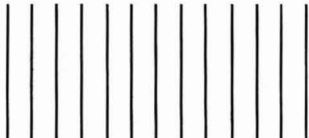
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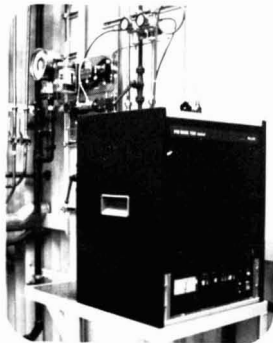


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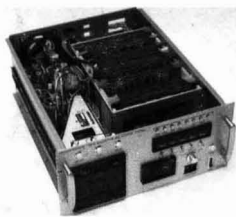


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