

Environmental

Science & Technology

FEBRUARY 1972

Noise: environmental insult 124



FROM THE CLEAN WORLD OF FRAM

THE NATIONAL AUTOMOTIVE TROUBLE QUIZ/A TV Special, March 26*

*Check local listings.

Fram waste treatment systems for industry

From initial studies through design, construction and operation...FRAM will work with your staff...or independently...to perform any of the steps required to solve your waste water problems. Look to FRAM for a creative system, competitively proven for any of the following applications:

- Color Removal
- Oily-water Separation
- Sanitary Waste Treatment for Marine and Land Environment
- Secondary and Tertiary Waste Treatment for Industry
- Pollution Control for CPI

...plus many other innovative ideas to help make it a clean world.



For some fast action and comprehensive solutions to your waste water problems, call 401-722-5000.

**INDUSTRIAL DIVISION
WASTE TREATMENT SYSTEMS**

750 SCHOOL ST., PAWTUCKET, R. I. 02860 (401)722-5000—BOX 50096 TULSA, OKLAHOMA 74150 (918)939-5451

Circle No. 6 on Readers' Service Card

Editor: James J. Morgan

WASHINGTON EDITORIAL STAFF

Managing Editor: D. H. Michael Bowen
Associate Editor: Stanton S. Miller
Assistant Editor: H. Martin Malin, Jr.
Editorial Assistant: Carol Knapp Lewick

MANUSCRIPT REVIEWING

Assistant Editor: Norma Yess

MANUSCRIPT EDITING

Associate Production Manager:
Charlotte C. Sayre
Editorial Assistant: Julie Plumstead

ART AND PRODUCTION

Director of Design: Joseph Jacobs
Production Manager: Bacil Guiley
Associate Production Manager:
Leroy L. Corcoran
Art Director: Norman Favin
Layout and Production: Dawn Leland

Advisory Board: R. F. Christman, G. F. Hidy, P. L. McCarty, J. C. Morris, David Jenkins, P. K. Mueller, Charles R. O'Melia, J. N. Pitts, Jr., John W. Winchester

AMERICAN CHEMICAL SOCIETY

1155 Sixteenth St., N.W.
Washington, D.C. 20036

Executive Director: Frederick T. Wall

Books and Journals Division

Director (Acting): John K. Crum
Head, Business Operations Dept.:
Joseph H. Kuney

Group Manager, Publications:
D. H. Michael Bowen

Assistant to the Director: Ruth Reynard

ADVERTISING MANAGEMENT

Century Communications Corp.
For offices and advertisers, see page 186.

Please send *research* manuscripts to Manuscript Reviewing, *feature* manuscripts to Managing Editor.

For author's guide and editorial policy, see April 1970 issue, page 303 or write Manuscript Reviewing. In each paper with more than one author, the name of the author to whom inquiries should be addressed carries a numbered footnote reference.

Features

124 Noise in the environment
by Peter Franken and Daniel Page
Bolt Beranek and Newman, Inc.

130 Instruments for water quality monitoring
by Dwight Ballinger, EPA

Outlook

118 Pilot projects point way to cleaner coke ovens
120 Deep well disposal—state of the art is primitive
123 U.S. may help small businesses finance cleanup

Special report

111 Air quality around the states

Departments

Editorial 103	New literature 178
Currents 105	Bookshelf 179
Industry trends 174	Meeting guide 181
New products 176	Professional consulting services 183
	Classified section 186
Current research contents 100	

©Copyright 1972 by the American Chemical Society.
EST ON MICROFILM: This publication is available on microfilm. For information, write to: Microfilm, Special Issues Sales, ACS, 1155 Sixteenth St., N.W., Washington, D.C. 20036
SUBSCRIPTION SERVICE: All communications related to handling of subscriptions, including notification of CHANGE OF ADDRESS, should be sent to Subscription Service Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036. Change of address notification should include both old and new addresses, with ZIP numbers, and be accompanied by mailing label from a recent issue. Allow four weeks for change to become effective.
SUBSCRIPTION RATES 1972: Members, domestic and foreign, 1 year \$6.00; nonmembers, domestic and foreign, \$9.00. Postage: Canada and Pan American Union, \$4.00; all other countries, \$5.00. Single copies: current issues, \$1.50; rates for back issues or volumes are available from Special Issues Sales Department, 1155 Sixteenth St., N.W., Washington, D.C. 20036. Claims for missing numbers will not be allowed if received more than 60 days from date of mailing plus time normally required for postal delivery of journal and claim. No claims allowed because of failure to notify the Subscription Service Department of a change of address, or because copy is "missing from files."

Those interested in joining the American Chemical Society should write to Admissions Department at the Washington Office.

Published monthly by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive Offices, Editorial Headquarters, and Subscription Service Department, 1155 Sixteenth St., N.W., Washington, D.C. 20036. Advertising Office: 142 East Ave., Norwalk, Conn. 06851. Second-class postage paid at Washington, D.C. and at additional mailing offices.

The American Chemical Society assumes no responsibility for the statements and opinions advanced by contributors to its publications.

Current research

Continuous system models of oxygen depletion in a eutrophic reservoir 135

L. P. Varga and C. C. Falls

Both natural and cultural eutrophication may be a problem in the future. Nevertheless, the assimilative capacity of a reservoir can now be predicted by several mathematical simulation models which were developed for the Keystone Reservoir, in North Central Oklahoma. Keystone is typical of most reservoirs in the Great Plains with the difference that the shoreline of Keystone rapidly is becoming urban.

Formation and degradation of aerocolloids by ultraviolet radiation 143

A. Goetz and O. J. Klejnot

Trace amounts of hydrocarbons in the air form aerocolloids which can lead to the formation of oxidants such as ozone. The yields of such materials can now be assessed using an ultraviolet cascade, an instrument for measuring the formation of aerocolloids. The effects of four parameters—uv light, humidity, nucleating matter, and ammonia—on the formations are discussed.

Reinvestigation of the Jacobs-Hochheiser procedure for determining nitrogen dioxide in ambient air 152

L. J. Purdue, J. E. Dudley, J. B. Clements, and R. J. Thompson

The Jacobs-Hochheiser method for ambient air sampling and analysis of nitrogen dioxide is the only practical method available for air pollution monitoring studies and networks, in which analyses must be delayed. When relatively long sampling periods (up to 24 hr) are required, the J-H procedure is preferred over the more common Saltzman procedure in which a fairly unstable azo dye is formed during sampling.

Environmental air analysis for ultratrace concentrations of beryllium by gas chromatography 155

W. D. Ross and R. E. Sievers

Analytical methods for the determination of ultratrace amounts of beryllium are needed because of its high toxicity. The gc method is more sensitive and reproducible than any other method; the instrumentation is relatively inexpensive, and the method can be conducted by trained technicians. In 14 urban samples, atmospheric Be concentrations ranged from 1.6×10^{-4} to $4.9 \times 10^{-4} \mu\text{g}/\text{m}^3$.

Mercury inhibition on lipid biosynthesis in freshwater algae 158

R. S. Matson, G. E. Mustoe, and S. B. Chang

Mercuric chloride and methyl mercuric chloride—two chemical species found in the environment—significantly inhibit the development of freshwater algae. Significant inhibitions with mercuric chloride start at concentrations below 1 ppm; with methyl mercuric chloride, it is even lower than 1 ppm.

Biopolymers of activated sludge 161

L. L. Wallen and E. N. Davis

Activated sludge from municipal waste treatment plants may contain useful materials. If such products have commercial value, then they might assist in underwriting the cost of sludge disposal. *Zoogloea ramigera*, the predominant species in sewage, produced a heteropolysaccharide from glucose.

Bromine and chlorine loss from lead halide automobile exhaust particulates 164

J. A. Robbins and F. L. Snitz

Most of the lead in urban atmospheres comes from combustion of gasoline containing antiknock compounds. Commonly used antiknock mixtures react with lead in the engine combustion chamber to form lead halide particles that are emitted in the exhaust. The loss rate from bromine is much greater than for chlorine during the first half hour; no difference in the rates of change of composition was found between dark vs. sunlight.

Communication

Filtration of ferric hydroxide 169

G. A. Lewandowski and H. B. Linford

Iron compounds are present in many industrial waste streams and can be removed by precipitation as the hydroxide. Five variables were studied which affected the rate of precipitation. Optimum conditions for filtration were pH 6.6, high iron concentration, and the use of sodium or potassium hydroxide rather than calcium hydroxide. Agitation and rate of base addition had no significant effect on the precipitation process.

Correspondence

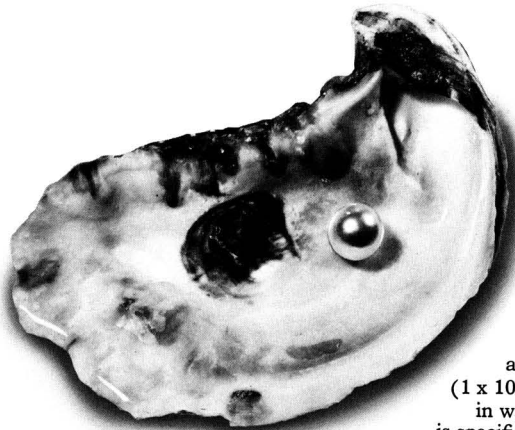
Attenuation of power station plumes as determined by instrumented aircraft 172

J. P. Friend
N. T. Stephens

One consideration which was overlooked in the earlier paper may perhaps invalidate earlier findings with regard to SO_2 decay in power station plumes. The authors contend that enough SO_2 is converted to particulate matter in the plume so that the assumption of the particles as a conservative tracer is grossly in error.

Photo credits: 107, Birmingham Alabama News; 110, Westinghouse; 112, John R. Shrader; 118, 119, American Iron & Steel Institute; 121, USGS; 122, Stan Miller. Cover: Joe Phillips

are you growing pearls?



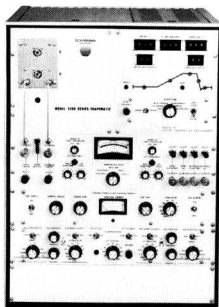
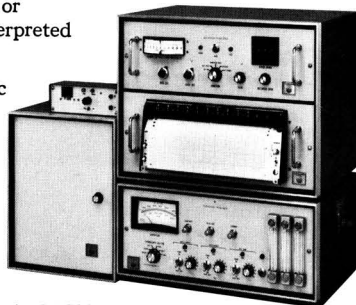
If so, nobody's likely to accuse you of polluting. But can you say the same about your process? You can with a DOHRMANN analyzer. It lets you take a hard look at any process that might cause environmental problems—*before* you get in trouble. "The DOHRMANN" determines total nitrogen, sulfur, or halogen in less than 5 minutes.

It's so sensitive you can detect as little as 40 parts per billion (1×10^{-9} grams) of total nitrogen in water. Because the system is *specific* for either N, S, or halogen, it provides easily interpreted quantitative results.

The DOHRMANN Microcoulometric Titrating System handles a wide range of materials—gases, high volatiles, liquids and solids. Natural gas, metals, pesticides, wastewater, seawater, or brine pose no problems.

Air contaminants? An ideal companion for the Titrating System is the DOHRMANN 2460 gas chromatograph which delivers separated constituents to the MCTS for rapid analysis. Use the two instruments together and you'll have a system that can't be matched for sensitivity and versatility.

Prices start at \$6500 for the MCTS and \$2125 for the G.C. For application notes, reprints, evaluation testing or ordering info contact DOHRMANN Division, Envirotech Corporation, 1062 Linda Vista Avenue, Mountain View, CA 94040. (415) 968-9710.

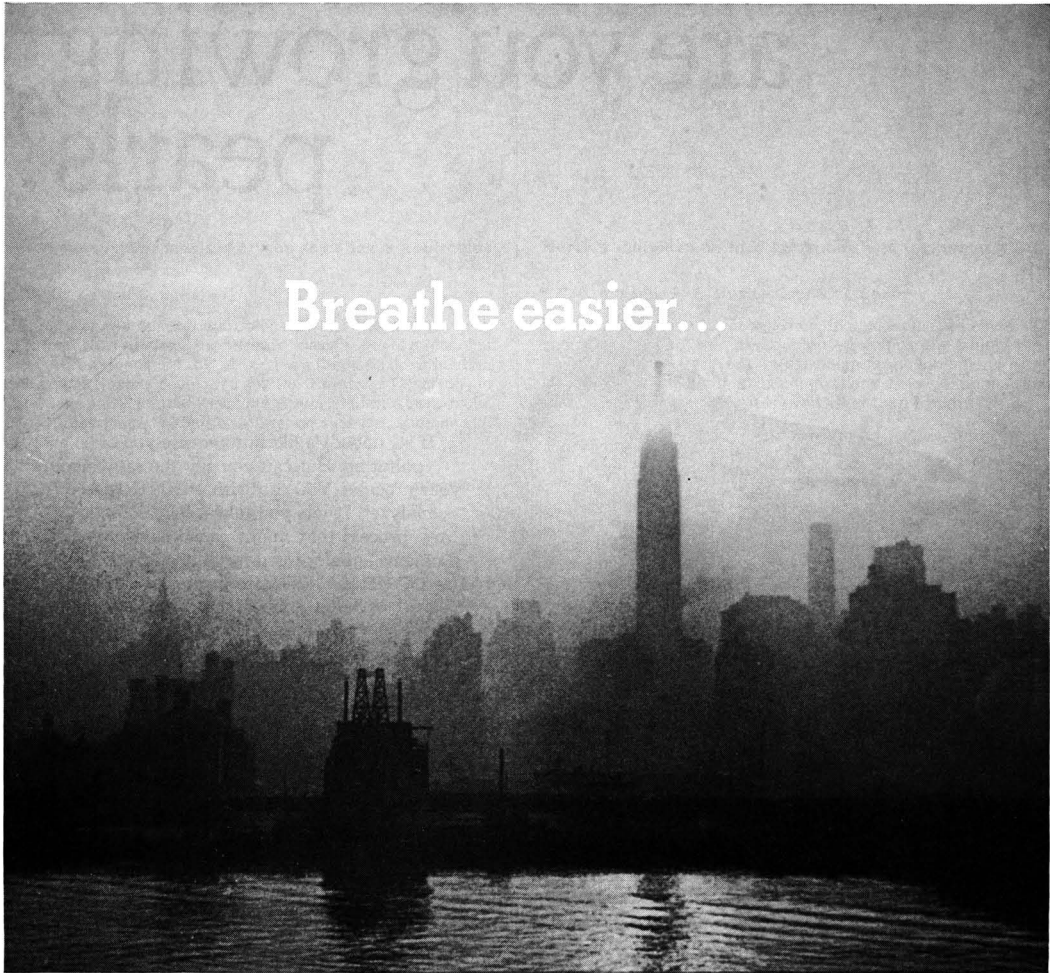


DOHRMANN
ENVIROTECH



TM

Circle No. 20 on Readers' Service Card



Breathe easier...

Matheson has gas mixtures for all pollution and vehicle emission studies

Study our list! Matheson has full availability of these important calibration mixtures in any suitable background: Carbon Monoxide...Carbon Monoxide & Carbon Dioxide...Hexane...Hydrogen Sulfide...Methane...Nitric Oxide...Nitrogen Dioxide...Propane...Sulfur Dioxide. These mixtures may be ordered in a wide range of cylinder sizes to meet your individual requirements.

Matheson has the technology to condition cylinders in a manner to provide stable analyzed mixtures — H₂S and SO₂ to the 0.1 ppm level. Matheson's improved analytical techniques — the most accurate partial pressure and volumetric techniques available — assure extreme precision and accuracy.



MATHESON GAS PRODUCTS

A Division of Will Ross, Inc.

East Rutherford, N.J.; Cucamonga, Calif.; Gloucester, Mass.; Joliet, Ill.; LaPorte, Texas; Morrow, Ga.; Newark, Calif.; Matheson of Canada, Ltd., Whitby, Ont.

Ready availability of these specialized products is another example of Matheson's continuing leadership in the preparation and analysis of gas mixtures. For more information on Matheson's capability in pollution and vehicle emission studies in particular and Matheson gas mixtures in general, fill out and mail the handy coupon.

22-70G

Send to Matheson Gas Products,
P.O. Box 85, East Rutherford, N.J. 07073

- General Catalog No. 27
 Your Guide to Gas Mixtures

Name _____

Firm _____

City _____ State _____ Zip _____

Circle No. 26 on Readers' Service Card

How clean is clean enough?

We are finding out rapidly how much cleanup will cost, but work on assessing the value of benefits is lagging

One of the burning questions of the day, it seems, is whether the cost of pollution control can be justified by the benefits a clean environment would provide. The whole idea of cost-benefit analysis has, indeed, taken on something of a sacred cow quality. It's an idea to which everyone pays lip service but about which there is a rather widespread ignorance, especially on the matter of how to quantify benefits. Costs, by contrast, appear rather straightforward to calculate; at least that is our conclusion in face of the reams of figures produced by organizations making sizeable control expenditures as a result of law or social pressure.

Given that clearing up air and water pollution would undoubtedly lead to tangible benefits for many people, an urgent task at hand is to compute the dollar value which can be assigned to each and every benefit. Cleaner air, for example, will lead to smaller laundry bills, smaller health care checks, and less damage to materials and vegetation. Cleaner water will result in natural recreational facilities being afforded which, if they had been built from scratch as community pools or artificial lakes, would have cost an identifiable amount of money. Shellfish industries worth a predictable amount might be started (or restarted). To calculate such benefits does not seem to be an insuperable task, although it will certainly be difficult.

The President's Council on Environmental Quality, in its 1971 annual report, appeared to support the notion that costs of pollution control can be more than balanced by benefits received by individuals and by the public at large. It has subsequently become obvious, however, that the administration does not buy the CEQ's conclusions. Hence we have had a series of warnings from administration officials, most notably from Commerce Secretary Maurice Stans, that the push toward a quality environment must not be allowed to go too far or too fast, lest in President

Nixon's words, "we seek ecological perfection at the cost of bankrupting the very taxpaying enterprises which must pay for the social advances the nation seeks."

The subject of costs and benefits is one of pivotal importance to the drive for a better environment. For if the dollar value associated with benefits resulting from cleanup could be shown to exceed the cost of cleanup, there presumably would be many fewer voices in high places advocating go-slow pollution control. If, on the other hand, cleanup costs grossly exceed any expected dollar benefits, then we surely ought to know that, too, so that we can extricate the matter of pollution control expenditures from the whole realm of economic rationalization and treat it quite separately—as we did the race to the moon. At the moment, all discussions of costs and benefits seem to be conducted in a never-never land of philosophical debate.

We are aware, of course, that there are many studies under way to quantify the cost of cleanup to a whole array of industries and other businesses (and that the government has over the years come up with some figures on dollar benefits). But we would still like to see efforts undertaken to compute benefits, efforts comparable in magnitude to those being made to compute costs. We fear that cost data alone may well be used to bolster contentions that control is too expensive to justify.

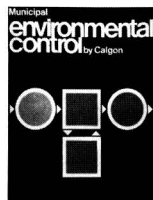
If the basis for answering Mr. Nixon's 1971 question: "How clean is clean enough" is to be economic in nature—and everything we have seen leaves little doubt that it is—then there is a great deal more calculation to do before *anyone* can give any sort of unequivocal reply.

D. H. Michael Bowen

Find out how we helped create this sparkling clear lake from a billion gallons of water. Sewage water.



Whether cleaning up sewage for reuse in a man-made lake—or simply working to upgrade operation of a city's sewage treatment plant—Calgon makes use of a unique approach to water pollution control. It takes our 14-page booklet, "Environmental Control," to give the complete story. Our systematic engineering approach can improve your wastewater treatment results and reduce costs. For a copy of "Environmental Control," write Calgon Corporation, Calgon Center, Pittsburgh, Pa. 15230.



The Water Managers



SUBSIDIARY OF MERCK & CO., INC.
Circle No. 24 on Readers' Service Card

WASHINGTON Corps permit program ordered to a complete halt

On December 28, the U.S. Army Corps of Engineers sent instructions to its 38 field offices declaring an immediate moratorium on the issuance of permits under the Refuse Act of 1899 (ES&T, December 1970, p 1101). The moratorium stems from a December 21 decision by Judge Aubrey Robinson of the U.S. District Court for the District of Columbia. Basically, the court made three points: • The permit program does not apply to nonnavigable streams • before the federal government issues permits for navigable streams, the determination must be made whether an environmental impact statement must be prepared • before any more permits are issued, the Corps must revise its regulations to reflect the ruling of the court. To date, 21 permits have been issued, and the Corps will continue to accept and evaluate applications.

EPA: performance standards and TT program

Performance standards for the first five industries were promulgated late last year with minor changes to the earlier proposed values (ES&T, September 1971, p 749). In the next two years, such standards will be established for 35–40 industries, but a second list of proposed standards will be published by this June, probably including the following industries—petroleum refiners, iron and steel mills, secondary lead smelters, asphalt batching, pulp and paper, aluminum reduction, nonferrous smelters, brass and bronze refining, and possibly sludge incineration. The technology transfer (TT) program, covering the aspects of air and solid waste in addition to water—was launched officially and is headed by Robert Crowe.

AEC: 1970 radioactivity release data & impact statements

The Atomic Energy Commission finds that the radioactivity released in gaseous and liquid effluents from nuclear power reactors during 1970 has been low in comparison with permissible AEC limits (for more on nuclear power, see ES&T, May 1971, p 404). It is not possible to view the year-to-year variation for any given plant because of fuel performance, reactor power production, and the extent to which treatment systems and analytical methods are used. Late last year, AEC made available reports concerning the environmental aspects of 33 nuclear power plants. After the reports are analyzed by the AEC regulatory staff, draft environmental impact statements will be prepared and made public.

National Academy reports on energy-environmental dilemma

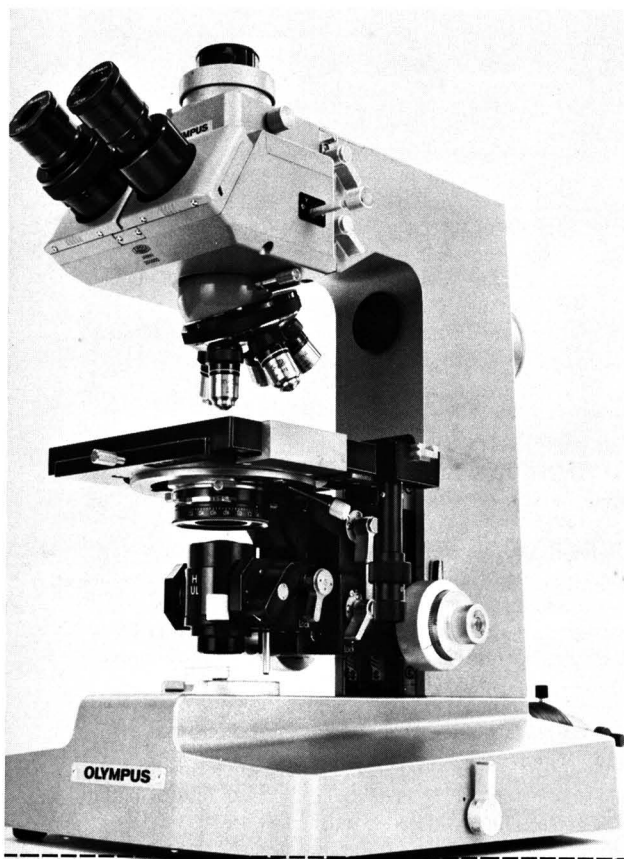
In a recent report, it is noted that better applications of present technology can minimize many power plant siting conflicts in the near future. Within the next decade, present technology will lead to satisfactory ways of handling sulfur-bearing fuels that will limit sulfur dioxide stack emissions to acceptable levels. But the report also notes that a wide variety of additional research—ranging from multimillion dollar development of a breeder reactor to the water temperature tolerance study of salmon fingerlings—is needed to fully resolve the dilemma. The report also calls for immediate action to simplify and consolidate the official approval process for construction and operation of new facilities to meet these demands.

Radioactivity release data for 14 commercial nuclear power plants

Oyster Creek (N.J.)
Dresden 1 (Ill.)
Nine Mile Point (N.Y.)
Dresden 2 (Ill.)
Humboldt Bay (Calif.)
San Onofre (Calif.)
Ginna (N.Y.)
Big Rock Point (Mich.)
Conn. Yankee (Conn.)
Saxton (Pa.)
Indian Point 1 (N.Y.)
Peach Bottom (Pa.)
Yankee Rowe (Mass.)
La Crosse (Wis.)

Meet fifteen new Olympus Microscopes: The universal research microscope AH/VANOX

Olympus meets change with change, and offers you the most flexible research microscope ever. Its rugged, modern, square-line stand contains a wide choice of application-oriented options that let you modify its configuration to suit your own use. You choose from four light sources, bright field or dark field contrast, phase contrast, fluorescence, from achromats to plan apochromats three stages, interference contrast—transmitted and reflected light. The new Olympus AH/VANOX modular concept increases your opportunities to build a system around your own requirements by providing a complete range of Olympus accessories. They include objective lens combinations and modular attachment camera systems that can be used with other Olympus microscopes. An economy without sacrificing quality. Find out how you can give your lab ultimate capabilities. Your Olympus dealer can give you more details, or send the coupon.



OLYMPUS

CORPORATION OF AMERICA

Send information on the AH/VANOX

On the complete Olympus line.

Contact me to set up a demonstration.

Precision Instrument Division, Dept. A-2
2 Nevada Drive, New Hyde Park, N. Y. 11040
(Telephone: 516-488-3880)

Name _____

Title _____

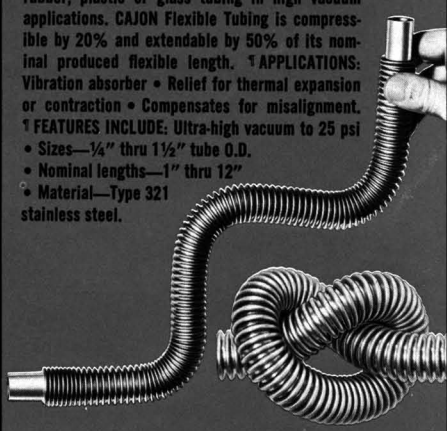
Address _____

CAJON[®]

STAINLESS STEEL FLEXIBLE TUBING

CAJON Flexible Tubing can be used in place of rubber, plastic or glass tubing in high vacuum applications. CAJON Flexible Tubing is compressible by 20% and extendable by 50% of its nominal produced flexible length. †APPLICATIONS: Vibration absorber • Relief for thermal expansion or contraction • Compensates for misalignment. †FEATURES INCLUDE: Ultra-high vacuum to 25 psi

- Sizes—¼" thru 1½" tube O.D.
- Nominal lengths—1" thru 12"
- Material—Type 321 stainless steel.

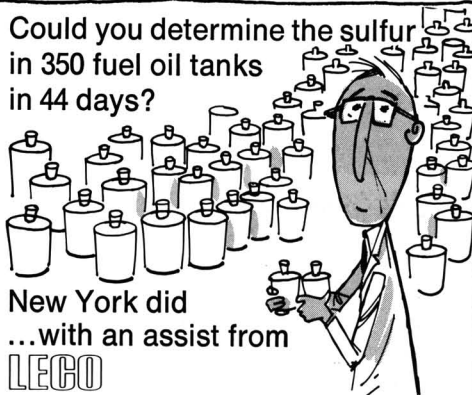


© 1970 by CAJON COMPANY/all rights reserved

CAJON COMPANY, 32550 OLD SOUTH MILES ROAD, CLEVELAND, OHIO 44139


Circle No. 1 on Readers' Service Card

Could you determine the sulfur in 350 fuel oil tanks in 44 days?



New York did ...with an assist from **LECO**

When New York cut allowable sulfur in fuel to 1%, the City's Dept. of Air Resources had only 44 working days to check out over 350 storage tanks . . . 309,000,000 gallons in all! This herculean task was completed by using the LECO Automatic Sulfur Titrator (ASTM 1552), which requires less than 10 minutes per analysis. Samples with sulfur content exceeding the 1% limit were rechecked by the bomb method (ASTM 129), which increased analysis time to two days. In every single case results agreed! If your pollution control program requires fast, accurate sulfur determinations, look into the LECO 10-minute Automatic Sulfur Determinator for dependable results in minimum time.



LABORATORY EQUIPMENT CORPORATION
3000 Lakeview Avenue, St. Joseph, Michigan 49085

Circle No. 22 on Readers' Service Card

← Circle No. 7 on Readers' Service Card

Enter your personal one year subscription to

Environmental Science and Technology

First journal in its field. Provides monthly information on research and technology involved in water, air and waste chemistry, as well as news of political and industrial aspects of environmental management.

Analytical Chemistry

Foremost monthly publication in the vital fields of chemical analysis. Treats both theoretical and applied aspects of analysis. Subscription includes special "ANNUAL REVIEWS" and "LAB GUIDE" issues.

Chemical Technology

One of the Society's newest publications. Serves chemists and chemical engineers charged with industrial innovation. Imparts immediate information of a pragmatic nature on a monthly basis.

- | | | | | |
|---|----------------------------|---|--|--|
| <input type="checkbox"/> ENVIRONMENTAL SCIENCE AND TECHNOLOGY | *ACS members
Nonmembers | <input type="checkbox"/> U.S. \$6.00
<input type="checkbox"/> U.S. \$9.00 | <input type="checkbox"/> **Canada, PUAS \$10.00
<input type="checkbox"/> **Canada, PUAS \$13.00 | <input type="checkbox"/> **Other Nations \$11.00
<input type="checkbox"/> **Other Nations \$14.00 |
| <input type="checkbox"/> ANALYTICAL CHEMISTRY | *ACS members
Nonmembers | <input type="checkbox"/> U.S. \$5.00
<input type="checkbox"/> U.S. \$7.00 | <input type="checkbox"/> **Canada, PUAS \$9.00
<input type="checkbox"/> **Canada \$11.00
<input type="checkbox"/> **PUAS \$19.00 | <input type="checkbox"/> **Other Nations \$10.00
<input type="checkbox"/> **Other Nations \$20.00 |
| <input type="checkbox"/> CHEMICAL TECHNOLOGY | *ACS members
Nonmembers | <input type="checkbox"/> U.S. \$9.00
<input type="checkbox"/> U.S. \$18.00 | <input type="checkbox"/> **Canada, PUAS \$13.00
<input type="checkbox"/> **Canada, PUAS \$22.00 | <input type="checkbox"/> **Other Nations \$14.00
<input type="checkbox"/> **Other Nations \$23.00 |

Payment enclosed (payable to American Chemical Society). Bill me. I am an ACS member.

NAME _____ POSITION _____

YOUR EMPLOYER _____

ADDRESS Home Business _____

CITY _____ STATE _____ ZIP _____

Employer's Business: Manufacturing Government Academic Other _____

If Manufacturer, Type of Products Produced _____

*NOTE: Subscriptions at ACS member rates are for personal use only. **Payment must be made in U.S. currency, by international money order, UNESCO coupons, U.S. bank draft; or order through your book dealer.

82
62

BUSINESS REPLY MAIL

No postage stamp necessary if mailed in the United States

Postage will be paid by

AMERICAN CHEMICAL SOCIETY

1155 Sixteenth Street, N.W.

Washington, D. C. 20036

ATTN: J. Medina

FIRST CLASS

Permit No. 1411-R

Washington, D. C.



environmental currents

STATES N.Y. will build underground waste treatment plant

New York City's Environmental Protection Administration has contracted Perini Corp. (Framington, Mass.) to build a \$228 million foundation for a \$750 million municipal water pollution control plant which will cover 28 acres, at or near street level. In fact, a park will be built on its roof. Construction is scheduled to begin this month; to be completed by 1976, the North Run plant will provide secondary treatment for 220 million gal of sewage from the west side of Manhattan, removing 90% or more of the organic pollutants.

Air pollution from fuel combustion regulated in N.J.

New Jersey regulations dealing with smoke from fuel combustion became effective last month. A no-visible-smoke restriction applies to equipment with an hourly capacity of less than 200 Btu gross heat input. Larger units, marine installations, and stationary sources may not emit smoke greater than 20% opacity, exclusive of water vapor. Diesel and construction equipment may not emit smoke greater than 40% opacity except for 10-sec periods (during stress or temporary power surges). Eleven other industrial firms have been cited for air pollution by the Dept. of Environmental Protection and have compliance deadlines this year.

Ill. accepts \$4 million abatement plan from steel company

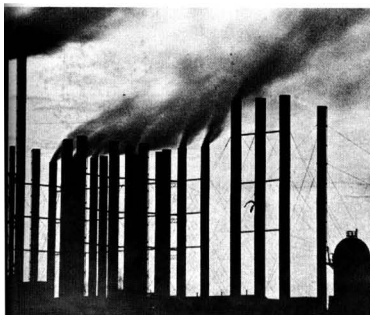
Illinois' EPA settled an air pollution complaint against Granite City Steel Co. by approving a \$4 million abatement program developed by the company. The program includes an advanced coke oven charging system (see this issue, p 118), sealing coke oven doors, a quench car water fogging system, and baffles installed in the quenching tower. EPA charged the steel company with air pollution law violations in 1967. (For more on pollution in the steel industry, see ES&T, October 1971, p 1004.)

Industry, government cooperate on oil spills

The Wisconsin Department of Natural Resources has developed (in cooperation with the Division of Emergency Government, local and federal authorities, and private industry) an interagency contingency plan designed to cope with spills of oil and other hazardous materials. An individual spotting a spill anywhere in Wisconsin can call the local fire or police department which will in turn contact the state government. On-scene commanders are on duty 24 hrs/day to minimize health hazards and damage to the environment.

Pennsylvania cracks down on surface mining

Effective last month, the Pa. Surface Mining Conservation and Reclamation Act prohibits surface mining without a license from the Dept. of Natural Resources, requires bonding (\$5000) and permits for individual operations, and sets minimum insurance requirements (\$100,000 total coverage for public liability, personal injury, and property damage). A \$500 fee is charged for a new license and \$300 for renewal. The act also applies to noncoal surface mineral extraction where more than 500 tons/acre/year of noncoal materials are produced.



Steel mill emissions

sample stack emissions accurately

with
the
portable

RAC TRAIN™
STAKSAMPLR



Designed and manufactured to EPA specifications, the RAC TRAIN STAKSAMPLR system takes accurate, low cost, isokinetic samples of gaseous and particulate emissions from chemical and combustion processes. This system's efficient performance—proved by years of operation and hundreds of units now

in service—meets the accepted standards for stack sampling.

Completely portable, the RAC TRAIN STAKSAMPLR system is designed for ease of installation and operation. It includes a nomograph that permits quick on-site calculations. For more information, write for BULLETIN 2343.

Our 25th Year



RESEARCH APPLIANCE COMPANY

Route 8, Allison Park, Pa. 15101

Export Office: 1505 Race St., Philadelphia, Pa. 19102

Environmental Instruments/Laboratory Products

Circle No. 21 on Readers' Service Card

TECHNOLOGY Overloaded sewage plant upgraded with oxygen

Pure oxygen is being used to improve treatment efficiency at an overloaded plant in Fairfax County, Va. Expansion of the county's Westgate plant, built in 1954 to handle 8 million gpd but now routinely loaded with up to 14 million gpd, involved addition of two 120-ft secondary clarifiers and compartmentalization and enclosure of existing tankage to comprise a secondary treatment area supplied with vaporized liquid oxygen. The oxygen system, designed by Engineering Science, Inc. and constructed by Air Products, Inc., is currently running at over 80% BOD removal (compared with about 50% historically achieved by the original plant). The new system takes over from an earlier chemical system involving use of ferric chloride and polymeric flocculant which was equally efficient in BOD removal, but which county authorities considered as relatively expensive.

Rented car emissions report issued

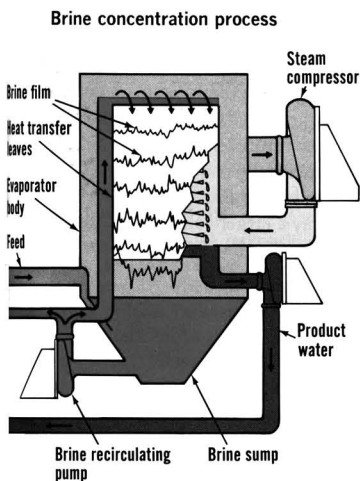
The scorecards are in for EPA's Rental Vehicle Surveillance Program, (see ES&T, April 1970, p 279). Results of 705 exhaust emission tests conducted on 1968 and 1969 model rental cars showed that most types of engines had emission levels below limits imposed by federal certification requirements. The sample represents about two thirds of the population of domestic automobiles for the model years examined. Based on the sample, about 75% of the '68-'69 population was projected to have hydrocarbon emissions lower than federal standards and about 60% had carbon monoxide emission levels lower than federal standards. Average mileage of the automobiles tested was 7,708 miles with a low of 29 miles and a high of 27,493 miles.

New desalting process receives commercial test

Resource Conservation Co. (Seattle, Wash.) has put the first commercial installation of its flat plate falling film desalination unit into operation in El Paso, Tex. where it will be used to purify brine blow-down from a compressor station on an El Paso Natural Gas pipeline. In the process, brine is heated to near boiling temperature, deaerated, and pumped to a sump at the base of the evaporative core. The hot brine is then pumped to the top of the core where it runs down the outside of hollow aluminum panels. The brine steams as it falls down the plates, and the water vapor is sucked out of the chamber, compressed slightly to raise its temperature, and then injected to the inside of the panels. The vapor condenses on the interior panel surfaces, giving up heat to the brine flowing down the outside of the panels.

Modified combustion procedures help cut NO_x

A combination of flue gas recirculation and two-stage combustion appears to be an effective technique for reducing NO_x emissions from stationary oil-burners. Flue gas recirculation can reduce thermal conversion of atmospheric nitrogen to NO_x to virtually zero, but has little effect on conversion of fuel-borne nitrogen, according to Esso Research and Engineering. Dual stage combustion—in which the first stage takes place at lower temperatures in a reducing atmosphere and complete combustion takes place in the second stage—cuts levels of both thermal and fuel NO_x. The optimum system would probably be one in which flue gas recirculation could be used to decrease temperature and thus thermal NO_x formation, while staged combustion would help check NO_x formation from fuel-borne nitrogen.



INDUSTRY Carbide markets controls for acid plant producers

Union Carbide is marketing two new molecular sieving processes for control of nitrogen oxide and sulfur dioxide from nitric and sulfuric acid plants. Union Carbide says its processes (PuraSiv-N and PuraSiv-S) cut oxide levels to less than 5 oz/ton of acid produced, surpassing any known commercial removal process for the industry. The processes exploit the adsorption and catalytic properties of Carbide's Linde Molecular Sieves to return oxides to the plant and increase acid production. There are now more than 350 sulfuric and nitric acid plants in the U.S. and two new H₂SO₄ plants, and five new HNO₃ plants will be built each year, according to federal estimates.

Computers aid in pollution control

Computers figure to be more important in pollution control. Westinghouse Electric has developed an automated system which can monitor and record weather and pollution data. The system records three pollution parameters in addition to time on a four-channel recorder. Tape from the recorder is electronically translated, processed, and analyzed by an ordinary digital computer. IBM has developed an experimental computer program which can accurately predict SO₂ concentrations in areas up to 1600 sq miles. In a recent test, the computer-assisted predictions, averaged over a 24-hr period, were within 15% or 0.05 ppm of actual conditions recorded in New York City during January 1971 when SO₂ concentrations were unusually high. The model is now being tested by IBM and the Allegheny, Pa. County Bureau of Air Pollution Control.

Role of consultants will diminish in future

Opportunities for independent consulting engineers in pollution control will become more limited in the next few years, despite the stepped up national effort to clean up the environment, says a report recently issued by Robert E. De La Rue Associates (Santa Clara, Calif.). Although the role and functions of consulting engineers within water pollution control has remained virtually unchanged during the last few decades, in the near future they will face more competition from engineering and design construction firms with the ability to do turn-key projects. Some equipment companies will also take on turn-key jobs, De La Rue says, and the government will play a larger role in specifying technology that will show the most return per federal dollar invested. (For more on turn-key, see ES&T, January 1972, p 20).

Ford starts up metal casting plant

Ford Motor Co. has formally opened its giant Michigan Casting Center, which spokesmen say has been designed to be the cleanest, most efficient casting operation possible with modern technology. The 2.6 million ft² plant contains some \$24 million worth of pollution control equipment, Ford says, and will eventually replace a 50-year-old foundry at the Rouge. The facility uses electric arc melting to recycle scrap for engine block castings, and has an extensive baghouse dust collection system designed to handle about 9 million ft³ of in-plant air per min. Noisy equipment is isolated with soundproof barriers, and cooling water will be recycled. Processes requiring electricity are computer-controlled to avoid high peaks in energy demand. The plant is expected to be in full production by the end of the year.



Monitoring pollutants

Air pollution over the states

ES&T Washington editorial staffers Stanton Miller and Carol Lewicke questioned state officials, zeroed in on issues, and learned that clean air in 1975 may be possible

It is a busy, hectic time for control officials. Never in the history of the nation's attack on air pollution has there been such a concerted effort at the federal, state, and local levels. Never before has so much progress been made in so short a time or has there been such real determination to get on with the cleanup job.

In fact, the goal of clean air by 1975—envisioned in the latest federal Clean Air Act—is a reasonable possibility, according to many state air pollution officials. (Although some believe the goal might be met quicker by relying on existing state regulations rather than on more roundabout federal requirements.)

There are 247 air quality control regions and approximately 4000 personnel on board today in federal, state, and local programs. It's estimated that \$23.7 billion will be spent in the five-year period 1970-75.

The responsibility for air pollution abatement is shared by federal and state governments under the mandate from Congress in the Clean Air Amendments of 1970 (P.L. 91-604). Together, they labor to get the job done, but states have principal responsibility for action, and, in practice, only they can solve their own problems.

The federal government provides an important backup role for the states. For instance, federal officials:

- assigned approximately 250 personnel to help states formulate implementation plans
- made available funding totaling \$1.5 million for necessary contract services such as emission inventories to help states complete their plans.

State and local officials, however:

- held hearings on implementation plans, most of which were scheduled late last year or early this year

- worked and cooperated with regional federal officials so that the necessary ingredients for a successful plan were included before submission.

Federal funds for air pollution control are running at a record high level, although barely one half of what they should be. The total number of personnel is approximately 4000 today, but more than likely will double by 1975. In January 1967, there were only seven federal officials in the regions; today, there are approximately 200.

To say that everything is settled and everybody is happy is, of course, oversimplistic. As always, there are some gripes; for instance, state officials point out that the nine-month lead time between promulgation of the national air quality standard and the submission date for implementation plans was cut in half. Another gripe is that there are regions where a pollutant other than the first half dozen so far specified in national standards is the main concern; in such regions, control of the first six pollutants must nevertheless take precedence. However, such differences do not detract from the fact that cooperation between state and federal officials is encouraging.

Implementation plans

A gut issue for air quality in the earlier federal clean air law, implementation plans remain a key issue under the amended statute. An implementation plan constitutes a control strategy—a combination of actions which when taken in the aggregate will achieve in a given region the degree of clean air specified in the national ambient air quality standards. The combination includes emission limitations, traffic controls, emission changes or charges, process alterations, revised management practices, and the like.

Last month, state officials submitted their plans for bringing emissions within their states to the level specified in the national standards. Federal officials now have till May 30 to review the 54 sets of plans—one from each state, the District of Columbia, Guam, Puerto Rico, and the Virgin Islands. If it finds a state plan unacceptable, the federal review team has an additional two months to come up with a substitute plan. In any case, by July 30, all plans must be approved.

Before any plan is federally approved, there are some 15-20 discrete elements that are examined, including:

- legal authority for the state to take action at different levels of air pollutants
- adequacy of emission inventory
- control strategy, the heart of the implementation plan
- adequacy of monitoring network
- adequacy of episode control.

Much of this review was performed at the EPA regional office level before the plans were submitted.

Without the services of 10 contractors, some plans would not have been completed in the designated time. Walden Research Corp. (Walden, Mass.) received \$80,000 for five contracts under which it performed emissions inventory studies for the states of Massachusetts and New Hampshire and the metropolitan area of Boston. It also helped with the implementation plans for Maine and Rhode Island. GCA Corp. (Bedford, Mass.) performed some work for a western state. Radian Corp. (Houston, Tex.) updated Louisiana's emissions inventory. (One of the problems there was that the inventory data did not agree with some of the state's on-line monitoring data.)

Nevertheless, at press time, one question on plans remains unanswered:

Will any governor request a one or two year extension, as permitted by law, in the achievement of the national air quality standards? Politically, it is unpopular; no one wants to be first.

Differences in plans

The problems with implementation plans differ in each state. The implementation plans due to date cover just the first half-dozen pollutants specified in national air quality standards; four of these pollutants are emitted largely from transportation sources—the main problem in some geographic areas. In other areas, it is stationary sources. In still others, it is a combination or a pollutant not yet specified in a national standard.

Approximately 60 cities have serious transportation problems manifested by a high ambient level of four pollutants—carbon monoxide, hydrocarbons, photochemical oxidants, and nitrogen oxides. In these cities, meeting the level of air quality specified in standards will be difficult. One contractor, TRW Systems, has been working out the transportation strategies for six of the cities. In Los Angeles, for example, hydrocarbon emissions must be cut 60% in order to meet the oxidant standard. One strategy might specify restriction of automobile traffic.

Some states had trouble meeting the deadline for submission of implementation plans. Alaska just started its program and was short of manpower. On the other hand, Illinois, with one of the better pieces of enabling legislation of any state, estimates that the budget for all components of its program is more than \$2.5 million. The Illinois program is well supported by government policy as well as by state and local funds.

Obviously, some states are ahead of others; some have had ongoing programs for years. Some are very good; others are trying their best. All are working, some perhaps for the first time. Most states feel that they will make the 1975 clean air goal. A few doubt that they can achieve that goal. Still others have reservations with regard to one or more specific pollutants in national standards.

Some officials doubt whether the automotive standards can possibly be achieved. Whether they can be is, of course, largely in the hands of the auto manufacturers. The Colorado air pollution official, Gerald Wood, believes that achieving these standards will require reducing engine size, reducing car

numbers, implementing vehicle regional transportation schemes in major cities, and total retrofit.

John J. Roberts, manager of the division of air pollution control in the Illinois EPA, is not encouraged that the federal EPA will continue to press the automotive industry to meet the mid-1975 emission standards. If the manufacturers do meet the emission standards, then Illinois will achieve both primary and secondary standards for all six air pollutants, says Roberts.

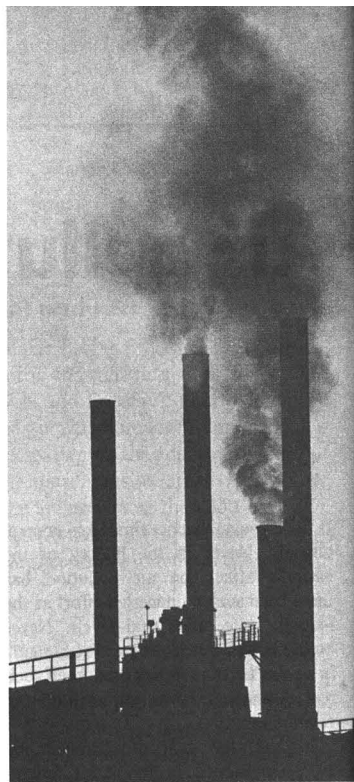
Maryland's Jean Schueneman believes that the air quality goal for the motor vehicle pollution complex of hydrocarbon-CO-photochemical oxidants will very likely be achieved as a result of the Federal program—but perhaps not by 1975. It seems pretty clear to the Maryland official, however, that this goal will be achieved by 1980.

Some officials doubt whether all the goals can be achieved. Alfred J. Eiguren, administrative director of the Idaho Air Pollution Control Commission, feels that it will be very difficult to meet federal ambient air quality goals by 1975. The Missouri official, Harvey Shell, doubts whether St. Louis will meet the automotive emissions standard in 1975, but points out that Missouri's air quality control regions are already below national standards except those for the automotive pollutants in St. Louis and for particulate matter in Kansas City and St. Louis.

Just because a state has had an on-going program for some time does not necessarily mean that it is ahead of other states who are gearing up for the first time. However, the views of those officials who have already been through the experiences are more valuable. Certainly, they seem more interesting.

California's George J. Taylor, chief of air sanitation, says, in his opinion, the deadlines set in the federal act for achieving national air quality standards are unrealistic in California. Several of the standards are so stringent, in fact, that it is questionable whether they can ever be achieved in metropolitan areas, he says.

In Alaska, achieving particulate matter and CO levels will cause problems. Thomas Hanna, an engineer in the State of Alaska Department of Environmental Conservation, says that Anchorage and Fairbanks have problems with dusty roads. In the summer, there is a strong possibility that the background particulate matter level is above the primary national standards limit. Solutions are expensive, he notes. Then,



Illegal? Such emissions may disappear as states work toward clean air goals

during the winter, Fairbanks has a CO problem, commonly referred to as an ice fog episode which usually lasts 10–20 days. Stagnation conditions occur at temperatures of approximately -30° to -60° F and inversions of 600 ft.

Modeling

Modeling procedures—the mathematical methods by which the total effect of numerous sources and meteorological conditions on air quality in a region is assessed—are not so elegant and reliable as to be the sole basis for developing programs to solve problems. In fact, most of them are inadequate. Despite this, modeling and testing of implementation plans have received considerable attention and federal funding. However, many state officials (for example, those in Maryland, New Jersey, New York, and Texas) are not sold on modeling.

With federal support, the Illinois EPA engaged Argonne National Laboratory to do detailed modeling and roll-back studies—what happens to the purity of air in a region as controls take hold—of three principal air quality

control regions—Chicago, St. Louis, and Peoria. As a result, numerous control strategies were tested and industry-specific growth factors introduced.

But even with a precise emissions inventory, the problems do not disappear. Idaho officials say it is difficult to translate emissions inventory data to an effective plan for reducing emissions to a desirable level. In fact, California's Taylor says that although we are studying modeling concepts and their applicability to our problems, we will probably not couple emissions inventories with modeling in order to translate the data into an implementation plan. South Carolina does not plan to depend on modeling either.

In Maryland, one of the major problems is how to incorporate air quality matters in overall land use and transportation plans for major urban centers. The New Jersey problem with modeling is that existing air quality in a portion of the state may be unacceptable due to sources outside of New Jersey. In such cases, it would be difficult to arbitrarily apply rollback to New Jersey sources, especially where standards are already severely restrictive.

In New York, only two air quality regions will be modeled. Just what problems will be faced in translating this into implementation plans is hard to foresee at this time, Alexander Rihm, the state official, summarizes.

Charles Barden says that Texas used the air quality display model for particulate matter in an eight-county area that included the city of Houston. Isopeles of existing concentrations and controlled concentrations have been completed and published in the draft plan. The controlled concentration verified the control strategy.

Tennessee officials don't see any problems in the modeling area, and Thomas E. Wright, an engineer with Rhode Island's air pollution control, has encountered no problem translating this data into an implementation plan.

Enforcement

Until recently it could safely be said that air pollution enforcement actions had taken a back seat to waste enforcement actions. Under earlier clean air bills, for example, only one federal action was taken. In that one, the Bishop Processing Co. (Bishop, Md.) was cited for odorous emissions. The time consumed in halting the pollution proved extremely lengthy and gave the federal action the appearance of a sham. This case pointed out the need for

streamlining enforcement procedures, which, in fact, are included in the Clean Air Amendments of 1970.

Already, one milestone has been reached under the new law. Last November, the federal government flexed its new enforcement muscle. It tested the emergency provisions which halt pollution activities when there is a threat to public health and found them effective. Under these provisions, 23 major industries were shut down in Birmingham, Ala., an area recently beset with two stagnation conditions. Simply, the EPA administrator obtained a court order to halt industrial production in this southern city until the stagnation conditions changed.

The states also can and have used their enforcement tactics against pollution sources within their jurisdiction. If a state fails to enforce its law, however, then federal enforcement procedures can be applied. And under the new law, enforcement actions at the federal level can be initiated for violating national air quality standards, performance standards, and so on.

Violation of the federal law carries the stiffest penalties—\$25,000 per day of violation, and one or more years imprisonment, or both. For a second knowing violation, the penalty increases to \$50,000 per day of violation, imprisonment for two years, or both. But it is really still too early to talk about enforcement actions under the federal law. Implementation plans have not yet been approved; they were only submitted recently. Performance standards for new stationary sources were finalized late last year. No plant has yet been built to which these standards specifically apply.

Violation of state and local rules and regulations can carry penalties ranging from a warning letter in virtually all states to a fine of \$10,000 per day violation in Alabama and Maryland. Other state penalties fall somewhere within this range. More importantly, perhaps, injunctive powers of many states provide more of an incentive for cleanup than straight penalties. Only state officials can solve state problems and even then, only if they are so inclined. Many are, and enforcement actions have been taken at the state level to halt air pollution.

In the industrialized states, the actions cover all possibilities. New York's Rihm says that there were 110 actions in the hands of N.Y. Counsel's office, as of October 4, 1971. They ran the gamut from failing to submit plans and open burning at municipal dumps, to viola-

tion of industrial process emission regulations. In Illinois, enforcement actions span the range from steel manufacturing pollutant sources to junk car burning, says John Roberts, manager of the air pollution control division which is responsible for enforcing regulations throughout the state.

New Jersey's William Munroe says that 1020 cease-and-desist orders were issued in fiscal year 1971. The state permits and certification system prevented approximately 51,600 ton/year of solid particles, 100,000 ton/year of sulfur compounds, and 2000 ton/year of solvents from entering the atmosphere, says Munroe.

Other states have taken action against open burning; in fact, most of the actions taken by Hawaii concerned open burning. Tennessee's Harold Hodges says two injunctive actions have been taken against municipalities for open burning. All told, 23 cases have been brought before the Tennessee Air Pollution Control Board. Colorado's Gerald Wood says that the state has approximately 80% compliance on stationary sources, and Colorado officials are moving to mass enforcement of open-burning regulations and waste disposal.

In Florida, there were 28 enforcement actions pending by middle of last year. Most such actions are handled at the administrative level. Florida has not yet assessed penalties for air pollution violations.

California's Air Resources Board does not normally engage in enforcement activities, since it is not really an enforcement agency. Nonvehicular sources of air pollution are controlled by 50 air pollution districts in California, 11 of which conduct active enforcement programs.

Schueneman says that Maryland has greatly accelerated its enforcement action since beginning in 1969. Most pollution sources are actively engaged in legally binding abatement schedules, explains Schueneman. Collectively, major individual sources in the state will spend approximately \$125 million during the period of 1969–1973 on abatement. This figure doesn't include increased fuel costs due to Maryland requirements for sulfur oxide emissions and particulate matter emissions.

Missouri's most illustrious success for air pollution control occurred last year when Union Electric reduced emissions at four plants, which will reduce sulfur dioxide ground level concentrations by 70% in downtown St. Louis.

The Texas air control board took action against 65 parties in the last four years and, last year, called a dozen hearings and issued 15 cleanup orders. Penalties, usually assessed on the basis of one violation per day (which is not a strict legal interpretation of the Texas Clean Air Act), ranged from \$50-\$1000 per violation. Legally, penalties could be assessed for more than one violation per day, Barden says.

In Alaska, New Hampshire, Rhode Island, and Virginia, no enforcement actions have been taken, which is understandable, since only recently did most receive a first set of regulations for air pollution controls. In fact, Virginia's state air pollution control board entered its enforcement phase only last year.

Monitoring networks

Most states have at least some phase of an air quality surveillance network that is required by federal law. Usually backed by federal funds, some networks even date back several years. On the other hand, a few states are just beginning to crank up their monitoring systems. The mere number of stations can be misleading for, perhaps, in not a single case are numbers comparable. Also, the varying topography and pollution sources vary from state to state. Per-

fect monitoring analytical systems, generally, are still not available that would be completely acceptable to EPA.

Due to the highly complicated topography and the dispersed nature of sources outside metropolitan areas, the Colorado monitoring network, consisting of 94 hi-vol stations plus 12 other instrumental stations, is presently being extended by a portable telemetered network for survey purposes. Illinois' network includes four multiparameter trailers, four continuous SO₂ monitors and numerous hi-vol samplers, dust fall buckets, and lead peroxide candles. This system is augmented by an eight-station continuous network operated by the city of Chicago, a four-station network operated by Cook County, and other local agencies during episodes and on an annual basis.

Hawaii's monitoring covers each county. Tennessee has 50 stations in 37 cities, and six continuous monitoring stations will be added (not including sampling networks in four metropolitan areas exempt from state control).

California's 70 continuous monitoring stations (35 of which are included in a statewide network) are federally supported. Missouri has approximately 60 monitoring stations, and volunteers gather the samples. Alaska does not have

a monitoring network yet; in fact, its first federal air pollution control grant was approved just last August.

New Jersey presently has 18 monitoring stations for sulfur dioxide, carbon monoxide, and smoke shade that telemeter the data to Trenton, the state capital. New Hampshire has 36 stations in operation and plans to expand (depending on federal funding). Rhode Island's two primary and 18 secondary stations will meet federal minimum requirements for an air quality surveillance network.

Florida's monitoring network covers the entire state, sampling particulate matter, sulfur dioxide, and other parameters. New York uses a computer-controlled system with 11 continuous monitors telemetering 14 parameters in addition to 200 manual stations (hi-vol samplers, sulfation candles, etc.). Wisconsin officials measure particulate matter at 61 sites. South Carolina's H. J. Webb says that the statewide sampling network, which has been operating for years, exceeds federal minimum requirements except for continuous sampling in a few rural areas.

Standards

The numbers game on standards has been played again and again. Certainly,

State officials

ALABAMA

M. T. Willis, Director
Alabama Air Pollution Control
Commission
State Office Bldg., Rm. 311
Montgomery, Ala. 36104

ALASKA

James A. Anderegg
Alaska Department of Environ-
mental Conservation
Pouch O
Juneau, Alaska 99801

ARIZONA

Norman E. Schell, Director
Air Pollution Control Division
4019 N. 33rd Ave.
Phoenix, Ariz. 85017

ARKANSAS

Jarrell Southall
Arkansas Pollution Control Com-
mission
1100 Harrington Ave.
Little Rock, Ark. 72202

CALIFORNIA

John A. Maga, Ex. Officer
Air Resources Board
1108 14th St.
Sacramento, Calif. 95814

COLORADO

Gerald P. Wood, Director
Air Pollution Control
4210 E. 11th Ave.
Denver, Colo. 80220

CONNECTICUT

Louis J. Proulx, Jr.
Air Pollution Control
79 Elm St.
Hartford, Conn. 06115

DELAWARE

John C. Bryson, Division Director
Division of Environmental Control
Tatnall Bldg., Capitol Complex
Dover, Del. 19901

DISTRICT OF COLUMBIA

Charles E. Couchman, Chief
Air Pollution Division
25 K St., N.E.
Washington, D.C. 20002

FLORIDA

Vincent D. Patton, Ex. Director
Department of Air and Water Pol-
lution Control
315 S. Calhoun St.
Tallahassee, Fla. 32301

GEORGIA

Robert H. Collom, Jr., Director
Air Quality Control Branch
47 Trinity Ave., S.W.
Atlanta, Ga. 30330

GUAM

O. Y. Natarajan, Administrator
Government of Guam
P.O. Box 2816
Agana, Guam 96910

HAWAII

Robert S. Nekomoto
Division of Environmental Health
P.O. Box 3378
Honolulu, Hawaii 96801

IDAHO

Alfred J. Eiguren, Administrative
Director
Air Pollution Control Commission
Statehouse
Boise, Idaho 83707

ILLINOIS

John J. Roberts, Manager
Division of Air Pollution Control
2200 Churchill Rd.
Springfield, Ill. 62706

INDIANA

Harry Williams, Director
Division of Air Pollution Control
130 W. Michigan St.
Indianapolis, Ind. 46206

IOWA

C. L. Campbell, Director
Air Pollution Control Division
Lucas State Office Bldg.
Des Moines, Iowa 50319

KANSAS

Howard Saiger
Division of Environmental Health
State Office Bldg.
Topeka, Kan. 66612

KENTUCKY

Frank P. Partee, Technical Direc-
tor
Air Pollution Control Commission
275 E. Main St.
Frankfort, Ky. 40601

LOUISIANA

John E. Trygg
Director of Environmental Health
P.O. Box 60630
New Orleans, La. 70160

MAINE

William R. Adams, Jr., Director
Environmental Improvement
Commission
State House
Augusta, Me. 04330

MARYLAND

Jean J. Schueneman, Director
Bureau of Air Quality Control
2305 N. Charles St.
Baltimore, Md. 21218

MASSACHUSETTS

James L. Dallas, Director
Bureau of Air Use Management
600 Washington St.
Boston, Mass. 02111

MICHIGAN

John C. Soet, Chairman
Air Pollution Control Commission
3500 N. Logan St.
Lansing, Mich. 48914

MINNESOTA

Edward H. Wiik, Director
Division of Air Quality
717 Delaware St., S.E.
Minneapolis, Minn. 55440

MISSISSIPPI

Jack H. Curry, Director
Air and Water Pollution Control
Commission
P.O. Box 827
Jackson, Miss. 39205

the numbers are not perfect—they never will be. But primary national air quality standards protect public health, and secondary standards protect human welfare. Most states have gone along with the numbers specified in the standards, but Arizona, Rhode Island, and Clarke County, Nev., have promulgated stricter primary standards, which is their option. Texas, Hawaii, Tennessee, Missouri, New Hampshire, and Florida have no gripes with the primary standard, but Illinois and New York with ongoing programs and perhaps more experience, do have complaints.

Most officials foresee no problem in meeting most standards by mid 1975, but many states may need a two-year extension in order to achieve the national oxidants standard, Texas' Barden says.

Thomas R. Hanna, an engineer with Alaska's air pollution department, objects to the numbers for particulate matter in the primary standard (75 and 260 $\mu\text{g}/\text{m}^3$) since they are described only in terms of mass concentration. He notes that health effects are directly related to particle size, so standards should be described in terms of respirable particulate matter. The Colorado official points out CO, NO₂,

and SO₂ standards are not related to altitude, and the total oxidants figure is common in Colorado forest valleys.

Illinois's Roberts and Idaho officials feel that national air quality standards are conservative. Maryland's Schuene-man, although he thinks the standards are fairly reasonable, says "we are particularly concerned about the short-term sulfur oxide standards (0.5 ppm for a 3-hr average) which along with other longer averaging time values for SO₂ does not seem to be adequate to prevent damage to vegetation, especially in the vicinity of major point sources of SO₂."

New York's Rihm says that most of the standards' numerical values were established from studies conducted under conditions with high concentrations of other contaminants as well as the contaminant of concern. He notes that many state officials feel that these standards are over-restrictive, and the excessive cost associated with controlling pollutants to these levels may not be warranted.

For example, Rihm notes that the standard of 75 $\mu\text{g}/\text{m}^3$ for suspended particulate matter was based on the fact that at 80 $\mu\text{g}/\text{m}^3$ adverse health effects began to occur (although the original study said that adverse effects occurred

in the range from 80 to 100 $\mu\text{g}/\text{m}^3$). The primary standard was therefore set at 75 $\mu\text{g}/\text{m}^3$, with an alleged safety factor of 7%. As for the sulfur dioxide standard, based on the statistical assumption that adverse effects would occur with 0.04-ppm annual average, the standard was set at 0.03 ppm with 25% safety factor.

Wisconsin's Becker noted that secondary standards are inadequately documented—natural background ozone may exceed the oxidant standard in many cases. South Carolina's Webb noted that even the criteria documents do not support the 60 $\mu\text{g}/\text{m}^3$ oxidant standard.

Regions

Of the 247 air quality control regions, 90 are interstate, and the remainder are intrastate. However, the concept of these air quality control regions seems to have been lost somewhere along the legislative road. For example, the entire state of Hawaii is one region. Alaska has seven regions, three of which are interstate. The entire state of Rhode Island and the southern portion of Massachusetts are encompassed in one air quality control region. All regions in Wyoming are intrastate. And so it goes.

Barden notes that of Texas' 12 air

MISSOURI

Harvey D. Shell, Ex. Sec.
Air Conservation Commission
112 W. High St.
Jefferson City, Mo. 65101

MONTANA

Benjamin F. Wake, Director
Division of Air Pollution Control
Cogswell Bldg.
Helena, Mont. 59601

NEBRASKA

Henry D. Smith
Division of Air Pollution Control
411 S. 13th St.
Lincoln, Neb. 68508

NEVADA

Richard Serdoz
Bureau of Environmental Health
201 S. Fall St.
Carson City, Nev. 89701

NEW HAMPSHIRE

Forrest H. Bumford, Director
Air Pollution Control Agency
62 S. Spring St.
Concord, N.H. 03301

NEW JERSEY

William A. Munroe, Chief
Bureau of Air Pollution Control
P.O. Box 1390
Trenton, N.J. 08625

NEW MEXICO

Richard Burgard
Air Quality Control Unit
P.O. Box 2348
Santa Fe, N.M. 87501

NEW YORK

Alexander Rihm, Jr., Director
Air Pollution Control Program
Department of Environmental
Conservation
Albany, N.Y. 12201

NORTH CAROLINA

W. E. Knight, Chief
Air Quality Division
P.O. Box 27048
Raleigh, N.C. 27611

NORTH DAKOTA

Lloyd Ernst, Chairman
Air Pollution Control Advisory
Council
State Capital
Bismarck, N.D. 58501

OHIO

Clyde Watkins, Acting Executive
Secretary
Air Pollution Control Board
1030 King Street
Columbus, Ohio 43212

OKLAHOMA

Robert V. Blanche, Director
Air Pollution Control Division
3400 N. Eastern Ave.
Oklahoma City, Okla. 73105

OREGON

Harold M. Patterson, Director
Air Quality Control Division
1400 S.W. Fifth Ave.
Portland, Ore. 97201

PENNSYLVANIA

Victor H. Sussman, Director
Bureau of Air Quality & Noise
Control
P.O. Box 2351
Harrisburg, Pa. 17105

PUERTO RICO

Cruz A. Matos, Executive
Director
Environmental Quality Board
P.O. Box 11785
Sanjurjo, P.R. 00910

RHODE ISLAND

Austin C. Daley
Division of Air Pollution Control
204 Health Bldg.
Providence, R.I. 02908

SOUTH CAROLINA

H. J. Webb, Executive Director
Pollution Control Authority
1321 Lady St.
Columbia, S.C. 29211

SOUTH DAKOTA

Robert Hayes
State Department of Health
Office Bldg. No. 2
Pierre, S.D. 57501

TENNESSEE

Harold E. Hodges, Technical Sec-
retary
Air Pollution Control Board
Department of Public Health
Nashville, Tenn. 37219

TEXAS

Charles R. Barden, Deputy Com-
missioner
Air Pollution Control
Department of Health
Austin, Tex. 78756

UTAH

Grant S. Winn, Chief
Air Quality Section
44 Medical Dr.
Salt Lake City, Utah 84113

VERMONT

Richard A. Valentinetti
Department of Health
P.O. Box 607
Barre, Vt. 05641

VIRGINIA

Edgar B. Boynton, Chairman
State Air Pollution Control Board
Ninth St. State Office Bldg.
Richmond, Va. 23219

VIRGIN ISLANDS

Pedrito Francois, Director
Division of Environmental Health
P.O. Box 1441
St. Thomas, V.I. 08001

WASHINGTON

Gerald O. Freeman
Department of Ecology
15345 N.E. 36th Street
Redmond, Wash. 98052

WEST VIRGINIA

Carl G. Beard II, Director
Air Pollution Control Commission
1558 Washington St., East
Charleston, W. Va. 25311

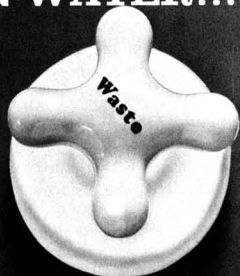
WISCONSIN

Brooks Becker, Director
Department of Natural Resources
Box 450
Madison, Wis. 53701

WYOMING

Robert E. Sundin
Wyoming Division of Health
State Office Bldg.
Cheyenne, Wyo. 82001

OIL IN WATER...



a pollution problem?

Solve It Through Continuous Field Monitoring or Laboratory Batch Measurements.

When you have a problem, turn to the experts... We at Teledyne are expert at systems and instrumentation to solve oil-in-water problems. Because the accurate measurements of oil in plant effluent water is one the principal forms of analyses of interest in determining waste water quality, we are pleased to provide information that may solve your problem.

Some principal problem areas:

- Soluble & Insoluble Oils
- Refinery Effluents
- Boiler Return Condensate
- Municipal Water Treating Systems
- Laboratory Applications

An example of Teledyne's problem solving is the advanced Continuous Oil Monitoring System, Model 660, employing a proven combination of sample conditioning and a unique analyzer to provide a total oil analysis of superior accuracy.

Teledyne's Model 670 permits a Laboratory Batch Measurement to be made in only three to five minutes!

Contact us for details.



**TELEDYNE
ANALYTICAL INSTRUMENTS**

333 West Mission Drive
San Gabriel, California 91776
(213) 283-7181

quality control regions, seven are contiguous with other states and four with Mexico. In the northern U.S., Michigan has regions contiguous with Canada. Whether states will adequately control air pollution to the extent necessary to achieve the national air quality standard on both sides of the border (state or country) remains to be seen.

Maryland's Schueneman thinks that the most knotty problem has been agreeing to appropriate attacks on pollutant emissions in the Washington, D.C. region. "We had hoped for uniformity, but it appears that this will not be achieved," he explains. The feds say that as long as ambient air quality standards will be achieved in the several parts of the region, uniformity of emission control programs is not necessary.

One problem with interstate regions is the usual problem of communication and coordination of effort. For example, New York has two interstate regions. Rihm notes that in one—with parts of New York, New Jersey, and Connecticut—the Interstate Sanitation Commission was designated as the coordinating agency for the region. In the other region—involving Vermont and New York—a coordinating agency isn't needed because no interstate problem exists. The region was originally created because of the International Paper Co. located in New York. However, when the region was created, the company was building an entirely new plant at a different site, and shut down the old plant. Idaho's one interstate region—northern Idaho/eastern Washington—also is not needed, according to the state's air pollution official.

What is important now is recognizing that state officials are responsible for achieving the standards. The 54 implementation plans are the real test under the law.

Industries

All industries are under the gun to clean up their emissions, and timetables for compliance are spelled out in the implementation plans. Whether or not specific industries meet their deadlines depends in most cases on a combination of economics, technology, and politics.

In many instances, technology is lacking. Every state has a problem with electric power generating plants. Technology has not adequately removed sulfur dioxide or oxides of nitrogen from such plants. Political solutions have failed in coming to grips with problems

of single-industry towns. Economics is the issue for industries operating on a slight margin of profits.

Problems vary from industrialized sections to rural areas. In some high-density urban areas, the problems do not even involve industry. In New York, for example, the major problems are associated with space heating, power production, motor vehicles, and refuse disposal.

Even if controls are technologically feasible, they may not be within the financial reach of small stationary sources. Large industries with specific problems can usually afford tight controls, but the supply of suitable alternative fuels is not available in sufficient quantities for complete fuel change-over.

Certainly, the deadlines mandated in the new clean air blueprint implies faith in technology, as exemplified by the auto emission deadlines.

Illinois's Roberts says that controlling industrial air pollution is an expensive although technically feasible proposition. The more troublesome sources which claimed no feasible control in the past, such as coke ovens (see *ES&T* this issue, page 118) and wet corn milling, can no longer do so.

In Alaska, two sulfite pulp mills are located in small towns. Abatement programs for these mills have hardly begun. Economics is the label here as it is in agricultural and related industries' pollution which plague the Colorado and Hawaii officials.

The phosphate mining industry and smelters are the two biggest problems in Idaho. In fact, in northern Idaho, there is a classic lesson to be learned in environmental control: A small town is dependent on a smelter that is a major source of SO₂ emissions. The plant installed a \$6.5 million control system that converted SO₂ to sulfuric acid—about 200 tons/day of acid with a corresponding reduction in SO₂ emissions of more than 70%. Due to the isolated location and unfavorable freight rates, the company virtually cannot give the acid away. The smelter cannot meet new standards without generating large amounts of acid that cannot be disposed of; economics may dictate a plant cutback or shutdown rather than incur a huge loss by distress rate acid sales. This emotional and political air pollution problem now faces the Idaho Air Pollution Control Commission.

Industrial air pollution control is relatively advanced in California, but fossil fuel power plants are still a serious problem. It is not technologically possible to control oxides of nitrogen

emissions well enough to meet standards in metropolitan areas.

Maryland's Schueneman says "We have received good cooperation from our industrial community and our fuel supply industry with some exception." Some Maryland industries are dissatisfied with the federal government's failure to promulgate forms and procedures for federal tax relief provisions for pollution control expenditures.

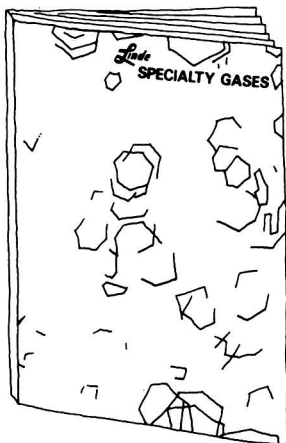
Schueneman also points out that satisfactory economical solutions for by-product coke ovens, flint glass production furnaces, certain galvanizing operations, desulfurization of stack gases, and control of nitrogen oxides (except from large combustion sources) seem to be "still quite sometime away."

In Missouri, wet corn milling operations in the grain industry and the charcoal wood industry are major air pollution offenders. Odors from large-volume operations in wet corn milling need both technological and economic solutions. Technology is not available to control emissions from batch-type operations in the charcoal wood industry (such batch industries are small operations with a low profit margin). Odor control problems of animal feedlots also need technological and economical solutions.

In New Jersey, Munroe notes that control solutions are needed for: spray paint operations in which the effluents are too dilute for economic control; chemical manufacturing which contributes intermittent odors from non-regular operations; petroleum refineries which produce intermittent odors resulting from residuals of past operations; and nonferrous metallurgical operations for which technology is not presently available for adequate control of particulate matter.

In Texas, cotton gins rendering plants, lumber mills, and asphalt plants emit air pollutants. Barden says that control technology for these operations have been available for some time, but economic considerations have imposed limitations on abatement progress. However, the channel carbon black industry, explains Barden, is an obvious example where controls are not yet available—there are only three such plants in the free world, and all three are in Texas. Carbon black is necessary for manufacturing aircraft tires, cosmetics, and drugs. However, the Texas Air Pollution Control Board has ordered compliance with regulations by December 31, 1972, which means that substitute products or processes must be found.

NOW, SOMETHING EXTRA IN SPECIALTY GASES.



FREE.
Linde's new
108-page
catalog.
The most
comprehensive
in the
industry.

Oh sure, we've always made more specialty gases than anyone else.

After all, Linde is a Division of Union Carbide, a corporation that's been making industrial gases for over 50 years.

But for the first time we combined the gases and the equipment and cataloged it all for you. Color-coded the sections, so you quickly get what you want.

And we *supply* what you want quickly too. Five hundred Linde Distributor locations nationwide provide fast service, but we mean really *fast* service. Cost-cutting FOB delivery too, because we have 5 plants across the country.

Linde's product know-how can even help you pinpoint your needs. Not just in specialty gases and types of containers, but in control equipment too.

They're all there in our new catalog. Our little something extra to help make your job easier. Send for your free copy today.



Linde is a registered trademark of Union Carbide Corporation

UNION CARBIDE CORPORATION
LINDE DIVISION, Dept. LB—EST
270 Park Avenue
New York, New York 10017

Gentlemen:

Please send me "the something extra" in specialty gases.

NAME _____
TITLE _____
COMPANY _____
ADDRESS _____
CITY _____ STATE _____ ZIP _____

Circle No. 16 on Readers' Service Card

Volume 6, Number 2, February 1972 117

outlook

Controlling emissions from coke ovens

The steel industry is putting lots of technical ingenuity into curbing pollution from one of its dirtiest operations

Soot, dust, fumes, dirt, grime, dark skies—all have been associated with the steel industry—and one of the dirtiest steel-making processes is coking. Coke itself is almost pure carbon, but the coal from which it is produced contains 20–32 wt % of other elements and compounds which are released as gases during the coking operation. Add the fact that 65 million tons of coke are produced annually in a total of 250 North American installations, and you have a wallop potential for air pollution.

Metallurgical coke, used as fuel in blast furnaces for making iron, is produced by controlled heating of soft coal blends. Until the early 1900's, "beehive" ovens discharged all volatile matter produced during the coking operation directly into the atmosphere. Since that time, "by-product" ovens have become standard and collect most of the volatile material for conversion into useful products.

In the coking operation, 16–20 tons of coal are charged or injected into the top of an oven, which is then sealed so that the coal bakes, rather than burns, at temperatures ranging from 1600–2300°F for about 17 hr. This intense heat releases volatiles contained in coal. These materials are piped to a chemical plant and treated to yield such products as gas, tar, and ammonia liquor.

A coke oven is a relatively small part of the iron- and steel-making complex—it's only about 40 ft long, 20 ft high, and 11–22 in. wide—and the 16–20 tons of coal put into each oven produce about 12 tons of coke. Therefore, coke ovens are built in groups or "batteries" containing any number of ovens.

On top of each battery is a hopper carrying car (larry car) that runs on rails in delivering coal into coke ovens through holes in the oven tops. Another

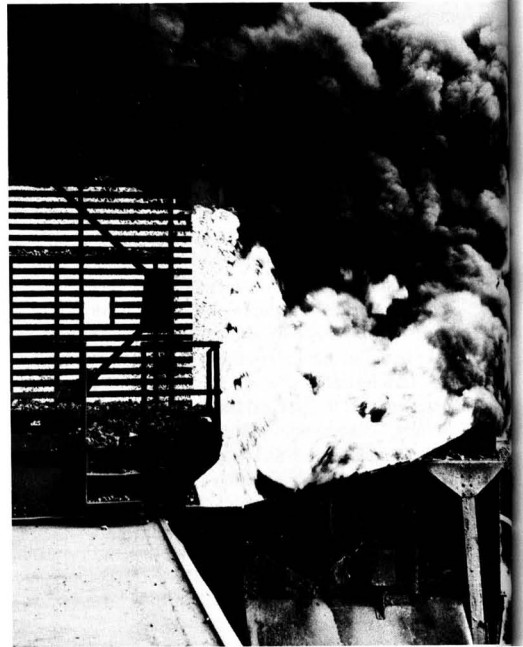
rail car (pushing car) runs beside the battery, levels the coal as it drops in an oven, and pushes the baked coke from the oven onto another rail car. This last car is then taken to a quenching tower where the coke is drenched with water to cool the material below the ignition point. The coke is then conveyed to the blast furnace iron-making process.

Environmental problems occur before and after the baking process. Gas and dust are released when coal is dropped into coke ovens, when the white hot coke is pushed from the oven, and when the coke is cooled by the water quench. These emissions may violate air quality standards and have also been linked with ailments of coke oven workers.

Charging

Charging a coke oven is mainly a manual task. The lids on top of the oven are removed by hand, and the larry car stops over the openings, releases coal from the hoppers in the car, and drops it into the oven. Because the oven interior is so hot (charging begins as soon as the previous batch of coke is removed), coal begins to burn immediately on entering the oven. Smoke and other pollutants are released into the atmosphere as coal drops into the openings and as the lids are replaced. Charging contributes the largest part of the emissions in the coking operation.

During the 17-hr coking process, lesser quantities of pollutants may be emitted from improperly sealed charging hole lids, oven doors, or other unsealed points. Coke oven emissions contain carbon monoxide, sulfur dioxide, hydrogen sulfide, hydrogen cyanide, and phenol, to name a few compounds.



Problem. *Pushing hot coke out of the coke oven contributes to the overall air pollution in coking operations (above)*

Solved? *Hopefully, one or all of the techniques discussed will result in coking with no accompanying pollution*

The American Iron and Steel Institute (AISI), the federal EPA, and various steel companies are supporting research to remedy this problem and others linked with coking. Design and construction of a \$1.5 million prototype system for smokeless charging of coke ovens has been sponsored jointly by the AISI and EPA for the past three years and will begin operation this month. The test facility is installed on the by-product coke ovens at Jones & Laughlin Steel Corp.'s Pittsburgh, Pa. works. If successful, the system will be offered to all coke oven battery operators in North America.

This smokeless charging operation maintains a vacuum in the ovens to hold smoke and gases in. The charging operator, in a sealed, air-conditioned car, will move along the battery while oven lids will be mechanically lifted, the hopper will be lowered over the opening, and the coal will be dropped. As the hopper nears the empty mark, a sensor will shut it, leaving a buffer of coal as a seal to prevent any smoke from coming out while the lids are automatically replaced. Meanwhile, a leveling bar will even the coal in the ovens.

The idea behind this is that if coal is fed into an oven through a sealed feed hopper and adequate suction is maintained by properly designed steam jets, pressure in the oven will never be positive during charging. There is a gas passage across the top of the oven into a standpipe, and suction provides negative pressure while the leveling bar is being withdrawn or when each charging hole lid is being replaced. In this way, AISI says all emissions during charging should be eliminated. One difficulty that is foreseen is how to maintain the delicate balance between air, coal, and heat to prevent combustion or explosion.

National Steel Corp. is hoping to solve the environmental problems in charging, pushing, and quenching by one complete system. The firm is adding to its old batteries in Granite City, Ill., and is

water recirculation and biological treatment of phenolic and cyanide wastes. The facility at Weirton is expected to begin operation this fall.

Another demonstration project, this time with a \$20 million price tag, is a coke pellet manufacturing process designed to eliminate coke oven emissions by eliminating coke ovens. Five companies—Bethlehem Steel Corp., National Steel Corp., Republic Steel Corp., Granite City Steel Co. (now part of National), and Consolidation Coal Co.—have collaborated on this project. A 500-ton/day demonstration plant is being built at Bethlehem Steel Corp.'s Sparrows Point, Md. operation.

Coke pellet (or formed coke) manufacturing is a closed system in that emissions are not given off into the atmosphere, as with the by-product ovens cur-

wet mechanical disintegrators or venturi scrubbers. CF&I Steel Corp. is presently installing this system in a new battery of coke ovens in Pueblo, Colo.

Charging coke ovens by pneumatic pipeline is another up-and-coming system for pollution control. Allied Chemical Corp. has installed a pilot plant in Ironton, Ohio to test the idea. Preheated coal (500°F) is transported via closed pipeline directly into the ovens. Allied officials say that smoke and gases from coke ovens will be reduced as much as 70% and coke production increased by as much as 50% by reducing coking time. Furthermore, emissions are reduced when the ovens are opened to remove the baked coke. The process also permits using lower cost, poorer quality coals to produce acceptable grade coke.

Pushing and quenching

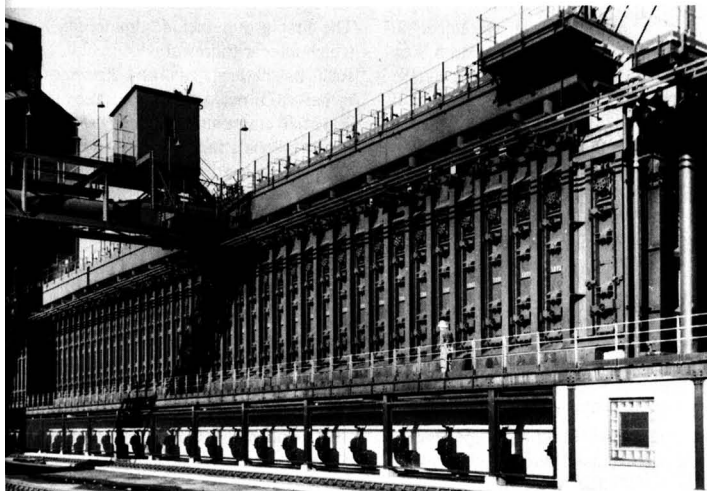
Although pushing and quenching are not as dirty as charging, they still create emissions that must be reduced. Sometimes this can be done in conjunction with reducing charging emissions—for example, AISI's smokeless charging or National Steel's self-contained charging.

Ford Motor Co. is attempting to reduce emissions from pushing operations at its 229 coke ovens in Michigan. The rail car that receives the hot coke from the ovens will have a hood-like covering tied into a long duct that will draft the effluent into a dust collection system.

Quenching can result in entrainment of fine coke particles in the steam plume from the quench tower. Also, water entrainment during quenching can cause "rain" on the downwind side of the plant. Baffles properly placed in quenching towers can, however, remove large water droplets and eliminate entrainment of coke dust almost entirely, and the plume is mainly water vapor.

Koppers has a trial system that tackles emissions from both pushing and quenching. The hot coke is discharged through a closed guide into a rotating kiln where quenching sprays cool the coke. Gases are exhausted through a scrubber.

Although most systems for controlling coke oven emissions are being used just on a trial basis, the steel companies, the federal government, and local citizenry, not to mention coke oven workers, are all hoping that a new clean look for coking operations is here to stay. CKL



building new coke ovens at its Weirton, W.Va. location. The new battery of 87 tall ovens is being equipped with controls to "satisfy every known air pollution problem associated with coking of coal," according to Fred Tucker, National Steel's vice-president of environmental control.

A completely self-contained charging system will use double collecting mains and a method known as charging on the main, a sulfur-removal system to produce elemental sulfur, an ammonia destruction system, oxides of nitrogen control system, and a closed system for coke pushing and underground quenching. The plant will also be equipped for

currently in use. The coal is heated in a fluidized bed, volatiles are removed during the conversion to coke, and the coke is then pelletized. In some cases, pitch recovered from the gas stream is used to bind together coke particles that make up the pellets. Besides reducing air pollution, pellet manufacturing is expected to use "high-volatile" coal and therefore stretch out dwindling supplies of the sought-after "low-volatile" coal with its low sulfur content.

The Koppers Co. and many European firms support the idea of collecting gaseous effluents in the larry car by adding equipment to each charging opening. The effluent is burned and washed with

Injection wells pose a potential threat

The unknowns of subsurface storage of wastes far outnumber the knowns; until the U.S. moves to curb such storage, it will likely become an even more popular practice

Not only is subsurface storage of wastes one of the newest techniques of waste disposal, it is, ironically, a form of potential environmental pollution. Industries, knowing full well that they no longer can put wastes into waterways, are turning to subsurface storage as one alternative.

It would seem that the public's attention to the practice is none too early, at least considering the facts:

- All told, there are tens of thousands of injection wells, more than 200 of which are used for injection of industrial wastes

- Each day about 10 million barrels of oil field brines are being injected into underground reservoirs from which no fluids are being withdrawn

- Each day the chemical industry is disposing of some 1 million barrels of aqueous waste solutions into 175 deep wells.

Disposal of man-made wastes underground has had various labels attached to it. They range from a "Frankenstein

monster" to an "unappraised resource." Without question, the number of such industrial subsurface disposal sites has doubled in the past decade and will more than likely redouble in the next. No federal regulation at present covers the practice; a handful of states either have or are considering regulations.

But information on which regulations might be based is lacking in the whole area of subsurface storage. At least, this was the consensus of attendees at the first national symposium on the subject. Billed as "Underground Waste Management and Environmental Implications," and held last December in Houston, Texas, the symposium was sponsored by the American Association of Petroleum Geologists (AAPG) and the U.S. Geological Survey (USGS). Additional support came from 20 technical associations, five federal agencies—including the Department of the Interior and the Environmental Protection Agency (EPA)—and one state agency—the Texas Water Quality Board (TWQB).

The symposium was attended by approximately 600 people, and 35 papers were presented on various aspects of the injection practices, the majority of them dealing with petroleum geology and oil brine injection experiences. Some were limited to radioactive disposal, while others dealt with the engineering aspects of construction of deep wells.

Scope

There are literally tens of thousands of wells for injection of oil field brines and for stimulation of oil flow from depleted wells. There are more than 200 wells for industrial waste disposal, although a precise estimate is not yet available.

"Underground space is an extremely important resource," said Vincent McKelvey, the newly appointed USGS director, in his keynote speech to the symposium.

"What must be realized is that underground space is not vacant space," said McKelvey. When wastes are injected they must, of necessity, displace other liquids and gases.

Two main questions that the new USGS director posed are:

- Can subsurface storage be used to solve our fluid waste problems?

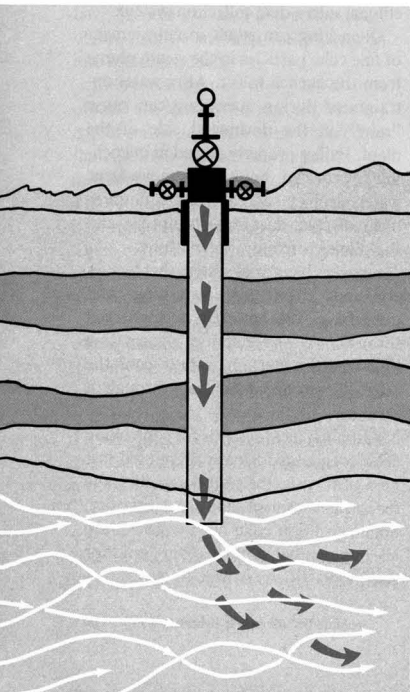
- Does the use of such subsurface space require the public oversight and federal, state, and local regulations? The answers are still in the making.

Basically, the uses of subsurface storage are divided into two categories. The first group includes materials for which later withdrawal is contemplated, such as natural gas and freshwater recharge. Of more obvious concern as a potential environmental threat are the other materials for which withdrawal is not contemplated. The materials in this second group are principally industrial wastes.

Regardless of possible hazards, underground space is being used today. In the eastern, midwestern, and Rocky Mountain states it is used for natural gas storage. In the Southwest, in Long Island, N.Y., and in California, fresh water harvested from runoff surpluses is used for recharge. In coastal areas, underground space is used for injection of treated or partially treated waters to stem the tide of saltwater intrusion.

Nevertheless, the unknowns of the practice far outnumber the knowns. The state of knowledge is primitive, at best. The simple fact remains that we cannot, with any sense of accuracy, calculate where the injected material is going, at least without undertaking extensive and costly tests. No one knows with any certainty where wastes have been injected.

As a start, USGS in fiscal 1972 is performing a study of present practices. The national survey on the status of subsurface storage and other basic research in cause-effect relationships



will cost \$1.2 million, but first results will not be available until the end of 1972.

Robert Stallman of USGS said in his technical overview at the symposium: "The available theories are either so simplified that they do not represent the real system adequately, or they are so complex that they have not been tested." Stallman elaborated, "I believe that the fundamental model of dispersion, as related to permeability and the potential field, is now the greatest deficiency in theory needed for prediction of effects due to waste disposal. A third area of technological weakness is the mathematical construction of predictive equations. Literally, all of our equations are based on the microscopic scale. Models based on the macroscale are needed."

Perhaps the most recent compilation of information on deep-well disposal is the USGS publication, "Water Supply Paper No. 2020." It contains 700 references on the subject and is available from the U.S. Government Printing Office, Washington, D. C. for \$1.50.

Federal policy

What is important is recognition of the fact that underground space is an extremely valuable resource, McKelvey reiterates. "It can be renewable or non-renewable depending on how it is used. For example, the consignment of subsurface space to storage of waste may make it a nonrenewable or a nonreusable resource. In contrast, the underground space would be both renewable and reusable when used for the temporary storage of an inert material."

Already there are federal regulations regarding subsurface storage on federal lands. For example, subsurface space for natural gas storage is sold or rented. McKelvey notes that under the Mineral Licensing Act, agreements have been reached for storage of natural gas on federal land in 15 locations in the U.S. "Others are being negotiated," he says.

On private lands, it is a different story. But it is becoming abundantly clear that the use of underground space must be regulated and monitored to protect the interest of others and to guard against damage to other resources.

Stanley Greenfield, the EPA assistant administrator for Research and Monitoring, noted in his symposium banquet address that the first mention of subsurface disposal in federal legislation occurs in the Senate-passed water amendments of last year (S. 2770). "In all current laws concerning water quality, the federal interest and author-

ity is only implicit in provisions concerning surface waters and public health service standards for drinking water supplies," he said.

Greenfield told the banquet attendees that "at the present time, we in EPA neither oppose nor promote deep-well waste injection. We regard it as an important technique with great possibility for both benefit and harm. And we feel that each injection project must be judged on its individual merits."

The present EPA policy on industrial injection wells is contained in a 2-page document. It was promulgated in October 1970, before EPA was formed, but Greenfield says that it is the policy that is strictly followed today and that he endorses it. Basically, the policy says not to use injection wells for wastes that can be treated. What can be injected are wastes that cannot be disposed of by an alternative treatment method.

It is important to note that the federal government is on record as opposing such waste disposal—"Without strict controls and a clear demonstration" that such disposal will not harm "present or potential subsurface water supplies...or otherwise damage the environment." The policy statement, Greenfield says, "concluded with a ringing declaration that we recognize subsurface injection as a limited technique—limited in space and in time—to be used with great caution and only until better methods of disposal are developed."

The assistant administrator explains that the EPA water quality research groups at Ada, Okla., and elsewhere are working out elaborations of the policy statement. In Greenfield's words, "They are trying to spell out the nuts-and-bolts specifications, to define what is adequate, practical, well-designed, and so on—all the policy's ambiguous, weasel words which everyone agrees to because they mean different things to different people."

State regulations

In the absence of federal regulations, a handful of states have enacted their own. But many state regulations are simply inadequate to control the underground space for wastes.

Only four states—Michigan, Ohio, Texas, and West Virginia—of those states that are members of the Interstate Oil Compact Commission have specific laws governing subsurface disposal of industrial wastes. Other member states, including Arkansas, Florida, Illinois,



"The uses of underground space are already diverse and are likely to become more so with the passage of time."

USGS Director McKelvey

Kansas, Missouri, Oregon, and Pennsylvania, have improved statutes. Sixteen other states are in the throes of developing policy statements and regulations. But the symposium attendee consensus was that no state law is exemplary. None would serve as the model for other states to emulate.

States that are nonmembers of the Interstate Oil Compact Commission are also making headway. These include California, New York, and Pennsylvania. In fact, ORSANCO—the Ohio River Valley Water Sanitation Commission (ES&T, January 1971, p 22)—is busily developing a law which may serve as a model for future regulation of injection wells.

Texas, a state with not only the largest number of petroleum geologists but more subsurface wells than any other state in the union, has experience in subsurface placement of materials dating back to 1936 with the East Texas Salt Water Disposal Co. In 1961, the Texas legislature passed the Injection Well Act, which was subsequently amended in 1965 and 1969.

At present in Texas, permits for injection wells must be obtained from the Texas Water Quality Board. Along with a \$25 application fee, the TWQB requires:

- a treatability study
- a list of adjacent landowners
- technical report including data on the geology, waste data, and aspects of well construction. Although the act does not require public hearings, the



"EPA of necessity is watching you."

EPA Asst. Administrator Greenfield

twqB routinely holds public hearings on its permits.

Since passage of the act, 100 permits have been issued in the past decade; 50 are active today, 10 were canceled, and the remaining 40 either have not been drilled or are not presently in operation.

Robert B. Hill of the twqB estimates that "more than 14 million gallons of industrial wastes are injected daily." He adds, "This represents a minuscule amount of the total industrial and municipal waste produced daily and discharged to surface drainageways."

Hill says that twqB receives 10-12 new applications each year. It renews its permits every five years. Recently, twqB has been asking permit holders to upgrade the use of wells—questioning whether the wastes could be treated, but this practice is just beginning.

Monsanto has spent \$3 million in subsurface injection in Texas alone. It started its first well in 1962 and a second one in 1965. Dow has five wells in Texas. Its first was put into operation in 1969 and there have been one or two new ones every year since.

Monsanto Pollution Abatement Manager Ronald Sadow says that his company's industrial wastes are pre-treated prior to injection. Usually, a pretreatment operation involves waste storage, separation of oil and/or suspended solids through flotation or gravity means, filtration through coarse sand or fine cartridge and diatomaceous earth, chemical fixation of pH, treatment to correct for corrosiveness or biological growths, followed by additional storage, and final pumping to the well.

Another Monsanto experience involves its injection well near Pensacola,

Fla. D. A. Goolsby of the USGS says, "Since 1963, more than 4 billion gallons of acidic industrial waste has been injected into a limestone aquifer." Although no pressure change has been noted in the overlying aquifer, pressure changes from 90 to 108 psi have been observed in two outlying monitor wells in the injection formation.

Effects

Although the final consequences of deep-well injection practices are far from clear, there are known experiences of earthquakes, land subsidence, and mishaps with existing wells. However, no generalization is possible; every case is unique (ES&T, August 1970, p 642). There have undoubtedly been mishaps, but it would seem that the notoriety of a few wells far surpasses the relatively innocuous experiences of others. For instance, tens of thousands of wells have been injecting oil brines without mishaps. And more than 200 industrial wells are operating without obvious problems today.

One of the first deep wells that received public attention was the 2-mile deep Rocky Mountain Arsenal well, near Denver, Colo. The well was drilled by the Corps of Engineers to dispose of wastes for which no other disposal procedure was available. One of the materials, for example, was a by-product from the production of a nerve gas. But the stimulation of earthquakes in the Denver area, for which the well was blamed (1962, 1963, and again in 1964-66) was certainly unpredicted.

The Earthquake Research Center (Menlo Park, Calif.) now has confirmed earlier suspicions that the Denver earthquakes were a function of time and injection. Still, the center has no predictive capability for forecasting future earthquakes, although studies are being made which may allow prediction.

Perhaps the most notorious mishap occurred at the Hammertill Paper Co. well at Erie, Pa. Between 1964 and 1968, approximately 55,000 barrels of spent sulfite wastes containing fibrous materials were pumped into the well under pressures between 1100-1300 psi. The well blew one Easter Sunday morning and spewed 150,000 gallons of wastes for several days into Lake Erie. What happened? The injection tubing corroded for one thing, and the so-called chemical heat problem was a second factor implicated in the failure of this well.

Another effect of wells is land subsidence—the settling of land masses.

In fact, land subsidence due to fluid withdrawal has been reported from many parts of the world. USGS spokesman J. F. Poland told the symposium attendees that subsidence develops most commonly in overdrawn groundwater basins, but subsidence of serious proportions also has been reported in several oil and gas fields.

The San Joaquin Valley of California is the area in the U.S. of most intensive land subsidence. More than 4000 sq miles are affected; in 1969, the maximum subsidence was 29 ft. Nevertheless, the rate of subsidence has been considerably reduced by injecting surface water in underground strata, according to this USGS spokesman.

Between 1917 and 1968, Poland continued, overpumping of groundwater caused as much as 13 ft of subsidence in the Santa Clara Valley and a decline in artesian head of some 180 ft. Water injected underground here has raised the water table 70 ft in four years and reduced the rate of subsidence to a few hundredths of a foot per year.

Looking ahead

As was made clear in the symposium, every subsurface injection case is unique. But the questions remain: How many wells should there be? What materials should be injected? It seems reasonable, although it may not be economical, that no industrial waste should be injected if it can be treated. But other questions, too, raise matters of policy. For example, human wastes logically might be put down wells in arctic environments. At least the current alternatives—filling drums with the wastes and scattering the filled drums across the arctic tundra—seem even less acceptable. Oil field brines have been injected for years with no mishap; certainly there would seem no need to halt this practice. And where else but underground could you store radioactive wastes? The AEC stores high-level wastes in containers that can be continuously monitored and in 1967 banned ocean dumping of such materials.

Under certain conditions, subsurface placement of materials may be practical and feasible, at least when all aspects of the interdisciplinary practices are known—the hydrology, the geology, and the engineering aspects of well construction. In the meantime, we must proceed with great care. In the long term, subsurface storage may yet prove to be the best, perhaps the only, way to dispose of the undisposable. SSM

Pollution and the small businessman

Pollution abatement requirements may hurt the small company more than the big corporation because it's harder for the little guy to find money for equipment

Building a successful small business or keeping a well-established one in good health is no mean feat in today's mushy economy. It's a task made all the more difficult by tightening pollution control laws. Installing pollution control equipment may make serious demands on a company's working capital, whether the business is a small foundry or a multinational conglomerate. But there's an important difference: Small businesses generally do not have access to the major money markets available to big companies.

Yet the country depends heavily on small business for a wide range of products and services. The overwhelming majority of U.S. businesses are small (see graph). Taken together, small businesses employ a sizable segment of the total labor force and account for a major portion of the GNP. It is estimated that there are some 300,000 small manufacturing firms in the U.S. alone.

The federal government, through such agencies as the Small Business Administration (SBA), seems intent on preserving a place for small business in the economy. Small business, for example, is given preferential treatment in some government procurement contracts. But SBA has no specific environmental program. Under the present system, SBA would be no more likely to lend a small business money for pollution control equipment than would, say, a neighborhood bank.

Likewise, the U.S. Environmental Protection Agency (EPA) has no special machinery to deal with the pollution problems of the small businessman, although the agency does set aside some procurement contracts for small businesses.

Help from the Hill

Nevertheless, there is good reason to believe that the small businessman may soon be getting some help from the Congress, at least as far as water pollution is concerned.

Both the Senate-passed Federal Water Pollution Control Act Amendments of 1971 (S. 2770) and the House counterpart (H.R. 11896) contain language which would establish a special loan fund, administered by SBA, to help small businesses meet water pollution control standards. And while S. 2770 has drawn sharp fire from the administration over several sections of the bill, there seems to be no objection to the small business loan provision.

Basically, the proposed law would

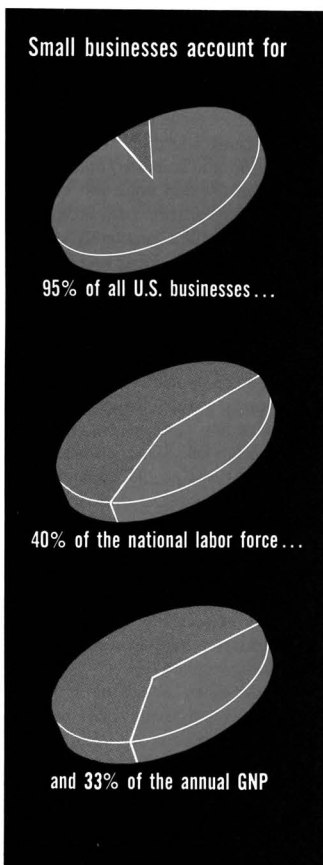
amend Section 7 of the Small Business Act by establishing an \$800 million loan fund. The fund would be used to help purchase pollution control equipment that a small business might be ordered to install as a result of tougher legislation. Loans could be made up to \$500,000 or up to 100% of the cost of the projects, whichever is less, and would be repaid over a 30-year period. Interest rates would be set at 2 percentage points below the cost to the U.S. Treasury of making the loans—in current terms, the rate to a borrower would be about 4%.

Under the plan, EPA would certify that an applicant's cleanup plan was necessary to comply with water pollution regulations. SBA would then determine whether or not the applicant would face "substantial economic injury" without the loan and judge the ability of the applicant to repay.

For the purpose of obtaining a loan, a small business would be roughly defined by SBA as a firm that is independently owned and operated and not dominant in its field, with an average employment limit of 250 for manufacturing concerns.

There is ample precedent for the type of financing described by the proposed law. Similar amendments to the Small Business Act were made in connection with passage of the Coal Mine Safety Act, the Occupational Health and Safety Act, the Wholesome Meat Act of 1967, the Wholesome Poultry Products Act of 1968, and the Egg Products Inspection Act of 1970, to help the small operator to meet new federally imposed standards. These precedents as well as the proposed fund for water pollution control are likely to be exploited for other pollution control measures as well. Sen. Gaylord Nelson (D.-Wisc.) who wrote the provision into the water bill recently told the Senate that he intends to introduce similar legislation for air pollution control.

HMM





Noise in the environment

Noise is not a necessary evil, and noise pollution problems can be solved. But like other pollution problems, the solution demands a blend of technology, public and private action, and healthy doses of economic realism.

One of the reasons that noise pollution has assumed its present proportions is the widely held and mistaken belief that nothing can be done about noise. But noise can be controlled, and much of the technology required for noise control is presently available. By properly applying existing technology, advance planning, and appropriate considerations in designing vehicles, machines, and buildings, a substantial amount of relief from noise could be provided at relatively small cost.

Noise pollution trends

Today, three related trends are focusing attention on noise pollution. First, noise is increasing and affecting more people. Second, the public is becoming more concerned about noise. And, third, acoustical specialists are stepping up their efforts to control the noise environment.

Noise has penetrated virtually every aspect of modern life and, generally speaking, the problem is getting worse. An ever-increasing number of common noise sources—motor vehicles, aircraft,

power tools, household gadgets—being put into use daily, and new noise sources such as snowmobiles and hovercraft are being added. New highways, new airports, and increased numbers of airplanes ensure that noise will be ever more widely distributed. Protection from this rising din is actually on the downswing due to increasing use of lightweight building construction and contemporary open plan designs.

This trend toward increased noise has fostered another trend: growing public concern, which is just beginning to emerge as a force to be reckoned with. According to a survey conducted for the Automobile Manufacturers, Inc., two out of three people questioned in the greater metropolitan areas of Boston, Detroit, and Los Angeles regard their neighborhoods as noisy places. Chicago has recently enacted a comprehensive and quantitative regulation designed to reduce noise pollution, and other cities and states are considering similar or regulatory actions.

Public concern about noise is beginning to be translated into action; for example, the noise argument against the supersonic transport and establishing the federal EPA Office of Noise Abatement and Control. The Environmental Protection Act requires that the environmental impact—including noise

effects—be assessed before proceeding on federally funded construction projects.

In direct response to the expanding noise problem and the growing public awareness, a third trend is now developing. Acousticians are attempting to make noise control procedures more understandable, more easily applied, and, hopefully, more widely used. Some examples of this trend are given later in this article.

Measuring noise impact

One of the difficulties encountered by anyone attempting to understand the nature of sound is the multitude of units and rating scales that can be used to measure sound. The great variety of units and scales has grown in part from efforts to achieve sophistication in measurement.

For most noise pollution situations, the A-weighted sound level, expressed in units of dB(A) or decibels, is most useful (Figure 1). The A-weighted sound level results from a weighting of the sound signal that gives greater emphasis to components in the mid-frequency region and less emphasis to components at lower and higher frequencies.

The science of psychoacoustics studies how the physically measurable prop-

Available technology could effectively control many of the present noise levels and sources

erties of sound relate to human judgments of "noisiness." Much work has been done to study human hearing responses so as to quantify, in a statistical way, how people react to different kinds and levels of noise.

Psychoacoustics has assumed increasing importance with the growing concern for noise pollution. Particular attention has been focused on assessing the impact of jet aircraft noise on communities near airports. A great deal of work has gone into the development of criteria for airport planning and of techniques for correlating human annoyance with such factors, as the sound level, the signal duration, how many flyovers occur, and what time of day they occur. One type of result is shown

in Figure 2. This describes projected 1975 operations at O'Hare International Airport, Chicago, Ill. Outside contour 30, land is said to be normally acceptable for residential housing, but hospitals, schools, and churches may require special construction to shield against aircraft noise.

Effects of noise

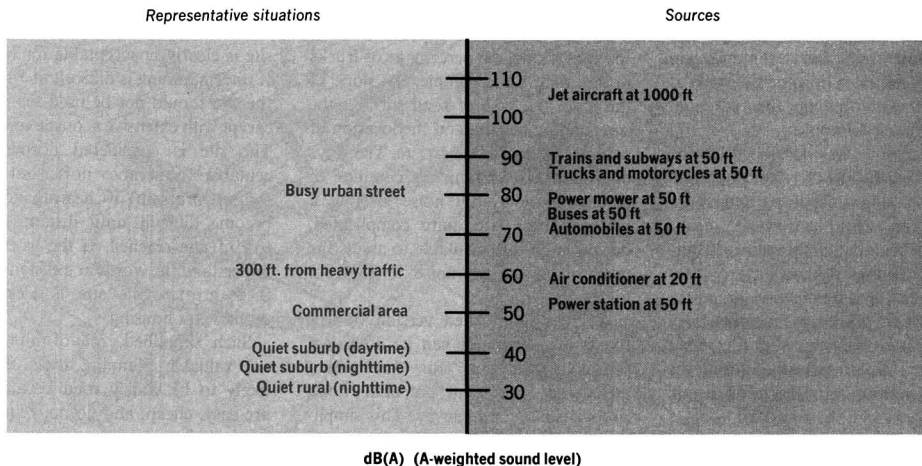
When one thinks about the effects of noise on man, probably the first thing that comes to mind is the loss of hearing that can result from exposures to very high noise levels. Brief exposure to levels of 140 to 150 dB(A) can rupture eardrums and cause permanent hearing loss. Longer exposure to lower noise levels can also damage hearing. On the

basis of available data, standards set under the Walsh-Healey Public Contracts Act now establish 8 hr as the maximum time that a worker can be exposed to noise levels of 90 dB(A) or more.

Noise levels high enough to damage hearing are usually not encountered in community situations. But even lower-level and shorter-duration noises that intrude into communities also have important effects. Speech interference is an easily demonstrable effect of lower-level noises. For situations such as listening to the radio or having a conversation, speech interference can be a distinct source of annoyance. For situations in which verbal communication is critical—commands shouted to the operator of a

Figure 1

Typical sources of community noise vary in intensity



wrecking crane, for example—speech interference can be a very real hazard. Noise can also disturb sleep and produce startle reactions in humans and animals.

The immediate effects seem to be relatively mild and short-lived. However, the longer-term effects of noise-induced annoyance are still a subject of much speculation. Careful and controlled scientific research is needed to determine what the long-range effects of noise really are.

Land-use planning

One of the most appealing approaches to the community noise problem is land use planning—establishing land use patterns that separate the most objectionable noise sources from noise sensitive areas.

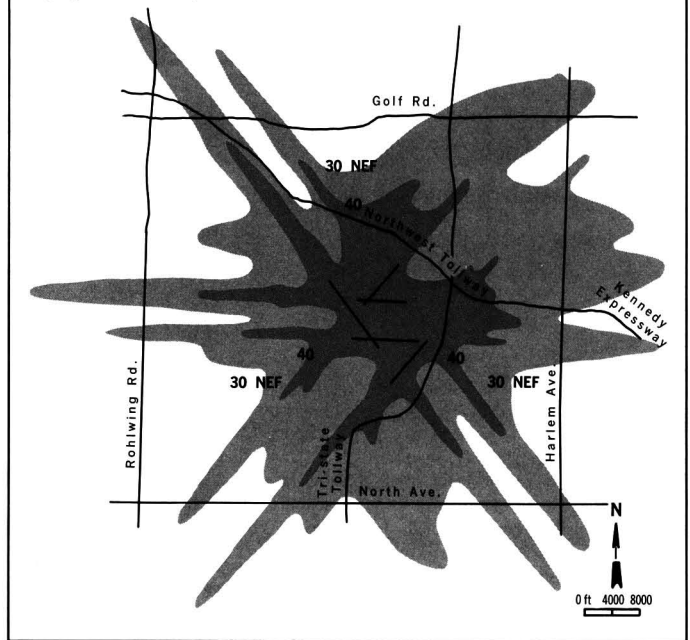
The noise levels for proposed airport, highway, and building sites can be predicted. An urgent need at present is to persuade planners, builders, and designers to use the available techniques for assessing the compatibility of proposed land use with the acoustic environment. One way to make acoustic planning tools more widely used is by developing highly simplified tests and screening procedures that enable persons with no background in acoustics to make “first-step” determinations of the acoustic suitability of proposed sites.

For example, the computational details involved in generating Noise Exposure Forecasts (NEF), like those shown for O’Hare International Airport, are quite complicated; indeed, a computer is usually required. But a greatly simplified version of the NEF techniques can furnish preliminary information that is useful in determining the potential severity of a noise problem.

The technique was developed for the U.S. Department of Housing and Urban Development (HUD) and is essentially an extrapolation of results previously computed for some 30 airports. It requires a knowledge only of the number of daytime and nighttime jet aircraft operations, the major runway locations and flight paths, and whether any supersonic aircraft will be using the airport. On the basis of this information, any airport can be assigned into one of four general categories for which the locations of the NEF contours are given. Of course, this simplified procedure

Figure 2

Noise intensity for O’Hare International Airport (projected for 1975)



provides approximate, though conservative, results; in cases where contours must be determined more precisely or where marginal errors can make a substantial difference, the complete NEF procedure would be required.

As another example of simplified noise estimation procedures for planning, consider highway noise. Noise surveys along roadways have shown that noise levels depend on a great many parameters, including the distance from the roadway to the observation point, the total volume of traffic, the average speed of traffic, the percentage of trucks in the total traffic volume, the slope of the road, the type of road surface, the surrounding terrain, and the location of natural and artificial barriers. The ways in which these parameters combine to make up the overall noise level at a given location are quite complicated, but programs are available to assess the resulting effects on noise levels from highways.

A greatly simplified version of this forecasting technique can be used as a screening procedure for determining areas that represent potential noise problems along a highway. This simplified procedure requires no acoustical experience on the part of the user and a knowledge only of the distance from the

roadway to the receiver, the number of cars and trucks per hour, and their average speed.

Another simple test uses speech interference criteria to rate the noisiness of proposed housing sites according to HUD’s interim guidelines. The test requires no special equipment, just a tape measure and two people. One person reads aloud from a book, and the other person moves away until he can only catch a scattered word or two in a 10-sec period. If difficulty in understanding occurs at approximately 7 ft or less, the site is clearly unacceptable for housing. If understanding is difficult at 7 to 25 ft, the site should not be used for housing except with extensive acoustic treatment. The site is considered normally acceptable (noticeable noise but not a serious problem) if hearing does not become difficult until distances of 26 to 70 ft are reached. If the listener can understand the words at a distance of 70 ft or greater, the site is clearly acceptable for housing.

Such simplified, rule-of-thumb tests are valuable planning tools that are likely to be widely used because they are easy, cheap, and do not require the services of an expert.

The obvious advantage of land use planning is that it prevents noise from

Table I. Urban areas list major noise sources

Source	Weighted %		
	Boston	Los Angeles	Detroit
Aircraft	17	16	5
Construction	2	1	
Industrial noise	<1		1
Motor vehicles	53	51	68
Other engine-powered equipment	<1	2	4
Radio and TV sets	2	3	1
Voices	14	8	13
Other noises	5	8	2
Not ascertained	6	10	5
Total	99	99	99

becoming a problem in the first place. The equally obvious limitation of land use planning is that it does not improve the existing noise situation.

Controlling the problem

As with other forms of pollution, the ideal place to control noise is at the source. If the source is sufficiently quiet, the rest of the problem is solved. Also, noise control often can be designed into a piece of equipment so that little or no compromise in the design goals is required. Noise control undertaken as a retrofit measure usually exacts a heavier toll.

Some of the major sources of noise nuisance as they were identified in the recent survey conducted for the Automobile Manufacturers Association are shown in Table I. The numbers associated with each source reflect the per-

centage of persons who cited a particular source as noisy, weighted by the extent to which they believe the source contributed to the city's total noise. Traffic noise was by far the worst offender, with aircraft and neighborhood activities also making substantial contributions.

What kinds of modifications could be applied to reduce the noise from the sources cited?

- Mufflers can control intake and exhaust noises of motor vehicles. Sound absorptive enclosures for engines and modifications to the engine design should provide further reduction—particularly for trucks and motorcycles. Additional research is needed to find ways of reducing noise generated by tires rolling over the pavement.

- Some of the recent aircraft, such as the 747, incorporated noise reduction technology developed in the last few years. Research sponsored by the U.S. Air Force and others is now being conducted to find new ways of reducing noise from jet aircraft engines. Sound absorbent linings at the intake and exhaust can reduce noise, but with some penalties of added weight and expense. Modifications to flight paths offer other possible, but partial, solutions to aircraft noise problems.

- Residential noise, which includes voices, radios, and tv sets, is not usually amenable to source modifications. However, modifications to residential buildings can isolate the noise.

- Mufflers and soundproofed enclosures could reduce noise from construction equipment by 10 to 40 dB(A).

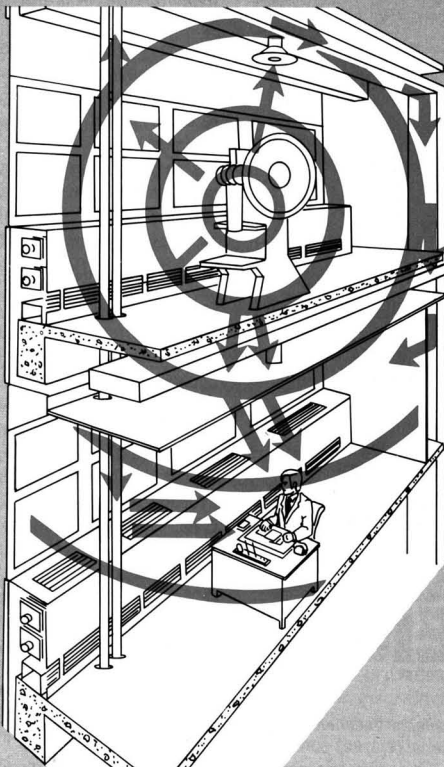
- Industrial noises can be a problem to persons working in the factory or plant as well as to nearby communities. The establishment of noise standards under the Walsh-Healey Public Contracts Act exerts some pressure on manufacturers to utilize equipment that produces less noise.

- The category of other engine-powered machinery includes such items as lawnmowers and snowblowers which often could be muffled with no great loss in performance capabilities.

Because the desired amount of noise reduction cannot always be achieved by good acoustic design at the source, modification of the noise path and receiver must be considered. Rerouting or

Figure 3

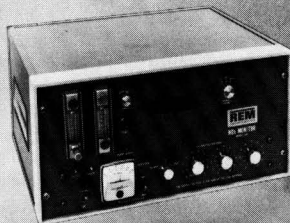
Noise travels many paths within a building



Our Competition is not even close...

Not when it comes to NO_x and ozone monitors. Our instruments are the *best* on the market. And we're prepared to prove it to you. If the features of our three instruments below do not convince you that they're the *best*, call us... we'll show you just *how* and *why* we think our monitors are so way ahead of their competition.

ATMOSPHERIC CHEMILUMINESCENT NO-NO_x MONITOR, Model 642



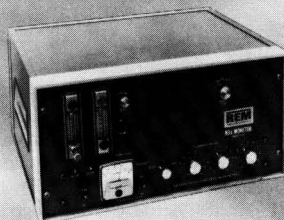
Atmospheric pressure O₃, NO chemiluminescent reaction • Instantaneous response to NO_x • Dry reaction — gas phase, chemiluminescent reaction (Ozone + NO_x) • Measures NO_x specifically • Differentiates between NO and NO₂ • No atmospheric interferences • Digital data display • Complete solid state electronics • Direct BCD telemetering capability and analog output for data recording • No vacuum pump necessary

ATMOSPHERIC OZONE MONITOR, Model 612



Measures ozone specifically • No atmospheric interferences (NO₂, SO₂, Cl₂, etc.) • Instantaneous response to ozone • Gas phase chemiluminescent reaction (ozone and ethylene) • Range of atmospheric monitor, 0-200 pphm (higher range available in industrial ozone monitor) • Digital data display • Complete solid state electronics • Direct BCD telemetering capability and analog digital output for data recording

VEHICULAR CHEMILUMINESCENT NO-NO_x MONITOR, Model 652



Atmospheric pressure O₃, NO chemiluminescent reaction • Measures NO specifically • Differentiates between NO and NO₂, and determines NO₂ by difference method • No atmospheric interferences • Instantaneous response to NO • Dry reaction — gas phase, chemiluminescent reaction (Ozone + NO) • Digital data display (4-digit nixie display) • Complete solid state electronics • Direct BCD telemetering capability and analog output for data recording • Self-contained unit, no vacuum pump necessary

For more information on why our NO_x and ozone monitors are the *best*, call or write:

REM
INCORPORATED

Instrumentation for Environmental Technology

2000 Colorado Avenue • Santa Monica, California 90404 • Phone: (213) 828-6078

Circle No. 29 on Readers' Service Card

relocation of noisy sources is one example of path modification—usually best applied in the planning stages in the cases of highways, airports, and trains. Another possible path modification is the use of walls and barriers to attenuate sound.

Obviously, noise intrusion into a building can be best combatted by sealing all outlets to the outside. In extreme cases, double structures can be used. Air conditioning, which becomes a necessity with windows sealed, may also be used within certain narrow limits to provide a background noise that covers up some other intruding noises. Special treatments, including the use of steel and lead panels, are available to prevent noise intrusion in certain cases. Gaskets around doors also can reduce noise transmission from one space to another. Inside a building, carpets, drapery, and acoustical tiles can provide some reduction of the noise levels in the building, although such internal treatments do not affect the noise intrusion from outside.

The many devious pathways that noise can take in traveling from one part of a building to another are shown in Figure 3. Although noise within a building can present an exceptionally tricky problem, it is a problem that can be solved.

High-rise buildings and their lightweight construction materials have created a particular noise problem in recent years. But the use of building techniques, such as floated floors and the incorporation of acoustically impervious partition materials can help to transform an acoustical horror into an entirely acceptable living space.

Regulatory steps

A regulatory program usually implies some form of legislation. Legislation against noise is nothing new in this country, and many states and major cities have general and qualitative laws against excessive or unwarranted noise. But the qualitative kind of law that was passed in Memphis, Tenn. in 1938 probably would not be effective today (even though Memphis won awards as the Nation's Quietest City each year from 1945 to 1960). Such laws are very difficult to enforce, because determining whether a violation has occurred is a matter of subjective judgment. Enforcement officials are reticent to enforce qualitative laws and courts are unable to prosecute.

Noise regulations can and should be objective, quantitative laws. Criteria

are well established for what noise levels are objectionable to a majority of people. Equipment and measurement procedures for determining when noise standards are exceeded are readily available, and their reliability is also well established. California, which has been a leader in establishing quantitative noise regulations for motor vehicles, enforces noise laws through highway patrolmen who have been trained to use a sound level meter to determine noise violations. The state has recently adopted a law that establishes standards for noise intrusion into communities near airports.

In New York City, noise intrusion into communities surrounding Kennedy, LaGuardia, and Newark airports is automatically monitored by a recently installed permanent monitoring system. New York City has also proposed a comprehensive noise ordinance of the kind recently adopted by Chicago.

Not only should laws be quantitative, but they must be specific as to the source of noise as well. A realistic law must recognize that a garbage disposal is inherently less noisy than a jack-hammer and assign limitations appropriate to each piece of equipment. To establish one absolute noise level not to be exceeded, regardless of what the noise source is, simply is not feasible, nor would it really solve the noise problem, because the annoying characteristics of noise depend on the background noise as well as the intruding noise.

Restrictions on where and how vehicles and equipment may be operated can also have a healthy effect on the acoustic environment. Different kinds of operational restrictions may have to be placed on aircraft, limiting the number of daily takeoffs in some areas or reducing nighttime operations. The operation of construction equipment may have to be limited to hours during the day when people are not trying to sleep or enjoy outdoor pastimes.

Another requirement for effective noise legislation is that it be consistent with current technology while recognizing that further reductions in the future are desirable. In the comprehensive Chicago noise ordinance, the ultimately desirable noise reductions are not required all at once, but in a gradual stepwise fashion up through 1980. The noise abatement program begins by a gradual phasing out of older and noisier devices that create the peak disturbances. Newer devices can then be phased in without imposing too great a burden on manufacturers or

operators of these devices. By introducing these requirements gradually, Chicago improves its chances of succeeding in its goals for a quieter city.

Legislation incorporating noise codes into building regulations could also be an important step. In the United States, New York is one of the few major cities with noise standards in its building code, although other cities are considering such standards. Such codes have been in existence in most European countries for many years.

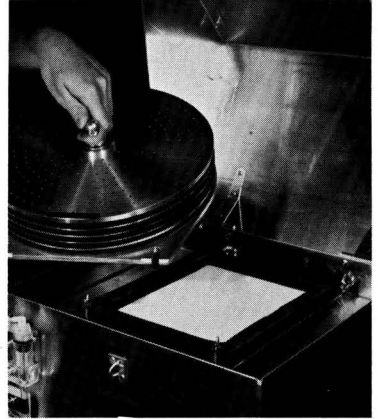
Control of noise pollution will require a public awareness both of the problem and of the potentials for solving it. Research and development have an important role to play in seeking new and improved ways of controlling noise. But what is primarily needed now is to begin applying, on a broad scale, the knowledge that is already available.



Peter A. Franken, *divisional vice-president of Bolt Beranek and Newman Inc., and director of the company's Architectural Technologies Division, holds a PhD in physics from Massachusetts Institute of Technology. Dr. Franken's most recent work is concerned with community noise pollution problems, and the assessment and control of noise from aircraft and surface vehicles. Address inquiries to Dr. Franken.*



Daniel G. Page *is a writer for Bolt Beranek and Newman Inc. Mr. Page is a 1960 graduate of Austin College, and was formerly on the editorial staff of the American Institute of Physics, associated with the Journal of the Acoustical Society of America.*



PARTICLE SIZING HEAD FOR EXISTING HI-VOLUME SAMPLERS



The Andersen Hi-Vol Head meets the current federal Ambient Air Standards plus gives sizing data in the following ranges:

- 7 Microns and Above
- 3.3 to 7 Microns
- 2.0 to 3.3 Microns
- 1.1 to 2.0 Microns
- 0.01 to 1.1 Microns

E.P.A. tests show excellent correlation between standard Hi-Volume Samplers and Andersen Head.

Adapts easily to existing Hi-Volume units.

For Ambient Air Sampling, Industrial Hygiene Studies, Mine Health and Safety Checks and Radioactive Tests.

Operates at constant 20 c.f.m. at 50 volts, increasing brush life more than 10 times.

2000 Inc. manufactures a full line of Viable, Non-Viable and Stack Sampling Equipment.

Consulting services are available.

* Andersen concept evaluated and approved by the Environmental Protection Agency.

For more details call or write:

ANDERSEN 2000 INC.
P. O. BOX 20769 AMF
ATLANTA, GA. 30320
PHONE (404-763-2671)
(formerly S.L.C., Utah)

Instruments for

Monitoring the environment is a fundamental part of the effort to define the nature and extent of pollution problems in order to develop an intelligent plan for abatement. Because of the movement of specific pollutants through the environment and the interaction between transport media, each medium must be monitored for a variety of substances and the data integrated to yield a comprehensive picture of the overall situation. Monitoring technology is defined by nature of transport media, pollutant sources, sample requirements, and necessary analytical methodology to produce an accurate result.

Methods used by the Environmental Protection Agency for measuring air pollutants have been described previously (see *ES&T*, August 1971, p 678). Research on analytical instruments and methods is carried out at the National Environmental Research Centers of EPA at Research Triangle Park, N.C. (air), the Perrine Primate Laboratory, Fla. (pesticides), the Western Environmental Research Center, Las Vegas, Nev. (radiation), and the National Environmental Research Center, Cincinnati, Ohio (water).

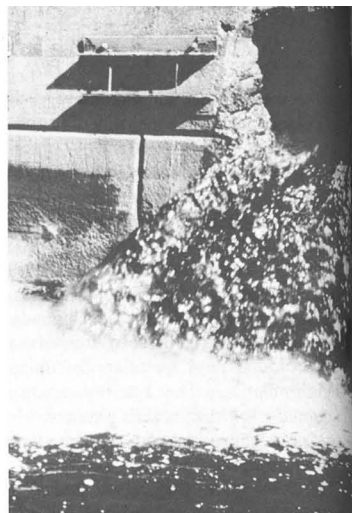
Monitoring the aquatic environment involves both measuring water quality characteristics in receiving streams and determining specific pollutants in waste discharges. A wide variety of tests are available, and the methods and equipment depend on the purpose of the monitoring program. Stream monitoring may be likened to ambient air monitoring, in that the measurements are made at a distance from the source of the discharge and are characteristic of a mixture of constituents from several unknown sources. These measurements indicate the exposure of the general population, either human or aquatic, and thus are often a good determinant of the conditions to be alleviated. Water

quality standards established by the states and approved by the federal government are designed to protect legitimate water users and do not directly indict a specific waste discharger. In contrast, direct measurement of waste effluent (source sampling) identifies the pollutant and the polluter and thus permits the application of abatement procedures at the source.

Refuse Act

Current attention in EPA is being directed toward source monitoring as a means of control. The Refuse Act of 1899 requires a permit from the U.S. Army Corps of Engineers for all industrial waste discharges to navigable waters in the United States. As a condition of the permit, the applicant must furnish data on 11 standard waste parameters [alkalinity, biochemical oxygen demand, chemical oxygen demand, total solids, total dissolved (filterable) solids, total suspended (nonfilterable) solids, total volatile solids, ammonia, Kjeldahl nitrogen, nitrate, and total phosphorus] and a selected group of additional measurements depending on the type of industry. Table I shows the additional requirements for Standard Industrial Classification (SIC) codes 26, 284, and 2871 as examples of the expanded list of waste parameters.

The required tests are designed to characterize the volume and concentration of the major waste constituents. The measurements listed above, when applied to all industrial discharges, permit comparison between treated and untreated effluents and indicate the degree of "damage" to the receiving water in terms of oxygen depletion, sedimentation, pH change, and nutrient impact. The additional measurements required (Table I) identify the waste contributions from specific industrial operations. Reporting these waste char-



Effluent. Waste stream monitoring may replace receiving water measurements

Table I. Examples of waste parameters sampled

SIC 26. Paper and allied products	
Color	Chromium
Specific conductance	Copper
Bromide	Lead
Chloride	Mercury
Sulfate	Nickel
Sulfite	Sodium
Phenols	Zinc
Total organic carbon	Total coliform
SIC 284. Soap, detergents, and cleaning preparations, perfumes, cosmetics, and other toilet preparations	
Color	Cyanide
Specific conductance	Sulfate
Turbidity	Sulfide
Oil and grease	Phenols
Chloride	Surfactants
	Total coliform
SIC 2871. Fertilizers	
Color	Cadmium
Turbidity	Chromium
Hardness	Copper
Oil and grease	Iron
Chloride	Lead
Fluoride	Manganese
Nitrite	Mercury
Pesticides	Nickel
Phosphorus-ortho	Zinc
Sulfate	Radioactivity
Aluminum	Total coliform
Arsenic	Fecal coliform

water quality monitoring

acteristics and volumes will show what is presently being discharged to U.S. waters.

Recommended analytical procedures for most of the measurements to be made in compliance with permit requirements are given in "Methods for Chemical Analysis of Water and Wastes, 1971"; microbiological procedures are given in "Standard Methods for the Examination of Water and Wastewater," 13th ed. (APHA); chlorinated hydrocarbon pesticides methods are described in "Methods for Organic Pesticides in Water and Wastewater"; while radiation measurement techniques appear in "Standard Methods" and in "ASTM Annual Book of Standards," Part 23, "Water, Atmospheric Analysis."

Aluminum, cadmium, chromium, copper, iron, lead, manganese, sodium, and zinc are analyzed by atomic absorption, although cadmium can also be measured by dithizone and zinc by colorimetric or polarographic methods. Arsenic is detected by colorimetric and nickel by polarographic methods. Cold vapor-uv is used for mercury. Some additional waste measurements and recommended methods of analysis are shown in Tables II and III.

In general, the procedures used provide reliable information on waste loadings. These methods have been in use for many years and have been thoroughly tested in many laboratories. The Environmental Protection Agency carries out an extensive program of methods research and evaluation to establish the reliability, precision, and accuracy of the procedures used in its water and waste laboratories. Examples of the range and accuracy of some methods are shown in Table IV.

The equipment and instruments required for these analyses range from simple to complex. Table V shows the

Table II. Physical, demand, and nutrient parameters and testing methods

Parameter	Method
Solids	Gravimetric
Color	Visual comparison
Turbidity	90° scatter photometer
Radioactivity	Gross α , β , ν , tritium
Specific conductance	Wheatstone bridge
Biochemical oxygen demand	5-day—20°C
Chemical oxygen demand	Dichromate reflux
Ammonia	Distillation-nesslerization or AutoAnalyzer
Kjeldahl nitrogen	Digestion-distillation or AutoAnalyzer
Nitrate	Brucine sulfate or AutoAnalyzer
Nitrite	Diazotization or AutoAnalyzer
Total phosphorus	Persulfate digestion or AutoAnalyzer
Phosphorus-ortho	Single reagent, stannous chloride, or AutoAnalyzer

Table III. Testing methods for organic and general parameters

Parameter	Method
Phenols	Colorimetric
Oil and grease	Hexane Soxhlet extraction
Total organic carbon	Combustion-infrared
Surfactants	Methylene blue active substance
Pesticides	Gas chromatography
Alkalinity	Electrometric titration or AutoAnalyzer
Bromide	Colorimetric
Chloride	Mercuric nitrate titration or AutoAnalyzer
Cyanide	Silver nitrate titration or pyridine pyrazalone
Fluoride	SPADNS with distillation or probe
Hardness	EDTA titration, AutoAnalyzer, or atomic absorption
Sulfate	Turbidimetric or AutoAnalyzer
Sulfide	Titrimetric or methylene blue colorimetric
Sulfite	Iodide-iodate titration

Table IV. Range and accuracy of test methods

	Optimum range, mg/l.	Accuracy, % bias
BOD	2-500	^a
COD	40-500	-4
Ammonia, nitrogen	0.05-2.0	-5
Nitrate, nitrogen	0.10-2.0	+4
Total phosphorus	0.01-0.5	+3
Chloride	10-400	-0.5
Hardness	10-400	-1
Sulfate	10-500	-3
Specific conductance	0.5-2000 μ mhos	-5
Arsenic	0.01-0.5	0
Copper	0.1-10	-10
Lead	0.1-10	-12
Mercury	0.2-10 μ g/l.	-13
Phenols	50-5000 μ g/l.	^a
Pesticides	0.01-0.2 μ g/l.	-20

^a True accuracy cannot be determined for these tests.

Table VI. Analyses can indeed be costly

Test	Analyst level	Typical charge/sample
pH		\$ 3-5
Alkalinity		\$ 3-12
Chloride	Technician	\$ 5-7
Solids		\$10-30
Specific conductance		\$ 3-5
BOD		\$30
COD		\$15-30
TOC		\$30
Cyanide		\$15-30
Phenols	Skilled analyst	\$15-30
Ammonia, nitrogen		\$ 5-15
Mercury		\$20-30
Metals		\$ 9-25
Pesticides		>\$50
Radioactivity	Expert	>\$50
Required parameters	Skilled analyst	\$129

type of tests and the instrumentation available for both laboratory and field measurement. It is apparent from this table that field equipment is lacking for the on-line measurement of many of the required waste constituents. As noted, the reliability of some of the available monitoring instruments has not been established to the satisfaction of the Environmental Protection Agency.

In contrast to air monitoring instruments, instruments for monitoring water often are designed to perform a number of test measurements simultaneously and record the results. Most of this equipment has been designed to provide stream monitoring rather than waste discharge evaluation. While the analysis method is the same in both situations, the concentration of the measured constituent is generally greater in the waste, and extreme sensitivities are not required. Interference, corrosion, and suspended solids are more significant in waste monitoring, requiring more rugged construction and modification of flow systems. It is highly desirable that manufacturers begin constructing equipment specifically for waste conditions, rather than assume that the same monitor will operate as either a stream or waste discharge instrument. Further, adapting process control devices commonly used in the chemical industry offers an excellent source of on-line waste monitoring equipment.

The primary restraint at the present time is the lack of reliable sensor systems for many of the chemical constituents to be measured in industrial wastes. A fertile field exists for developing sensors for the more complex tests necessary for proper waste characterization.

Since much of the analytical work for monitoring wastes must be done in the laboratory, consideration should be given to the cost of the tests. Table VI lists the type of determination, the relative skill of the analyst, and examples of commercial laboratory charges for performing the tests.

Producing reliable waste data requires careful application of the proper analytical methods, use of modern equipment, and an adequate program of quality control. The quality control program should provide checks on the reagents and gases used, the performance of the instrumentation, the care and skill of the

Table V. Reliability of some on-line instruments is not established

Parameter	Laboratory instrument	On-line instrument
Total organic carbon	Combustion-infrared	Yes ^a
Ammonia, nitrogen	AutoAnalyzer	Yes ^a
Total phosphorus	AutoAnalyzer	No
Chloride	AutoAnalyzer or electrode	Yes
Specific conductance	Wheatstone bridge	Yes
Copper	AA spectrophotometer	Yes ^a
Lead	AA spectrophotometer	Yes ^a
Mercury	AA spectrophotometer or mercury meter	Yes ^a
Phenols	Vis. spectrophotometer	Yes ^a
Pesticides	Gas chromatograph	No
Turbidity	Turbidimeter	Yes
Cyanide	Vis. spectrophotometer	No
Radioactivity	Counters and spectrometers	No

^a Reliability has not been established.

Available on-line water-monitoring instruments

Parameter	Manufacturer	Cost range
Total organic carbon	Ionics-Union Carbide Raytheon/AES	\$8,000-\$10,000
Ammonia, nitrogen	Technicon	\$5,000-\$10,000
Copper	Fischer-Porter Hach Chemical Co.	\$1,900-\$4,000
Mercury	Olin Corp.	\$20,000
Phenols	Ionics-Gulf (available 1972) Du Pont	\$4,000-\$7,000
Phosphate	Hach Chemical Co. Technicon	\$1,600-\$5,000
Multiparameter monitors, including chloride, sp. conductance, turbidity, and others	Enviro Control, Inc. Schneider Instrument Co. Raytheon/AES Ecologic Instruments Ionics-Union Carbide Robertshaw Hach Chemical Co. Delta Scientific Corp. Beckman Instruments, Inc.	\$5,000-\$15,000

Mention of companies or products does not constitute endorsement by the Environmental Protection Agency.

analyst, his ability to provide accurate results, and the proper reporting of the analytical answer. A formalized program to evaluate these variables and to establish the reliability of the data is highly desirable. Quality control charts, recording daily performance, and monitoring the output of each analyst have been found to be effective means of measuring and controlling the laboratory performance. A publication titled "Control of Chemical Analyses in Water Pollution Laboratories," soon to be distributed by EPA, outlines a quality control program for laboratories performing water and waste analyses.

Additional Reading

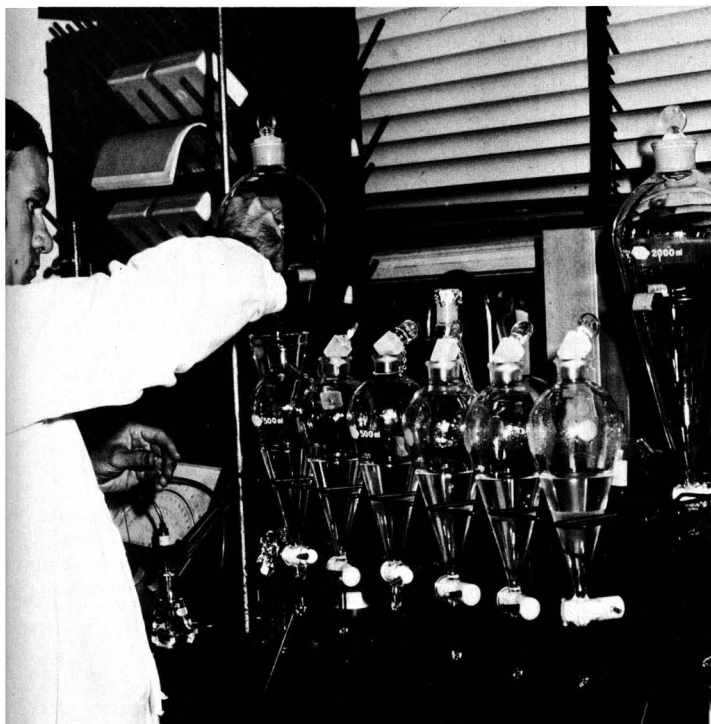
Hochheiser, Seymour, Burmann, F. J., and Morgan, G. B., "Atmospheric Surveillance—The Current State of Air Monitoring Technology," *ES&T*, 5, 678 (1971).

Application for Permit to Discharge or Work in Navigable Waters and Their Tributaries, Eng. Form 4345-1, Department of the Army, Corps of Engineers, Washington, D.C. 20314.

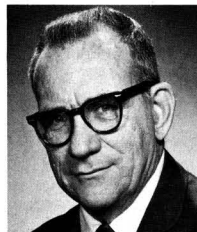
"Methods for Chemical Analysis of Water and Wastes, 1971," Analytical Quality Control Laboratory, National Environmental Research Center, Environmental Protection Agency, Cincinnati, Ohio 45268.

"Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association, 1015 18th St., N.W., Washington, D.C. 20036.

"1970 Annual Book of ASTM Standards," Part 23, "Water; Atmospheric Analysis," American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.



Analyzing. Tests, such as this one for extraction of organic waste samples, may become commonplace as more parameters are measured for water pollution control



Dwight G. Ballinger is director of the Analytical Quality Control Laboratory, part of EPA's National Environmental Research Center in Cincinnati. The laboratory is responsible for developing methods for water and waste analysis. Mr. Ballinger received his B.S. degree in chemistry from the University of Cincinnati and is the author of many publications on analytical chemistry of water and wastes.

WATER CHANNELLED IN RESOURCEFUL McGraw-Hill TEXTS

- 1. HYDRAULICS OF SEDIMENT TRANSPORT**
WALTER H. GRAF, Lehigh University. *McGraw-Hill Series in Water Resources and Environmental Engineering*. 544 pages, \$22.50

As a textbook for advanced undergraduate and graduate students, and as a reference work for engineers and researchers, this is one of the most comprehensive treatments of sediment transport available.

- 2. WATER RESOURCES SYSTEMS ENGINEERING**

WARREN A. HALL, University of California, Riverside and JOHN A. DRACUP, University of California, Los Angeles. *McGraw-Hill Series in Water Resources and Environmental Engineering*. 384 pages, \$13.50

An ideal source of reference for professionals in all levels and phases of water resource development, this book provides a timely and comprehensive discussion of both surface water and groundwater systems and their integrated usage.

- 3. ECONOMICS OF WATER RESOURCES PLANNING**

L. DOUGLAS JAMES, Georgia Institute of Technology and ROBERT R. LEE, Idaho Water Resource Board. *McGraw-Hill Series in Water Resources and Environmental Engineering*. 640 pages, \$16.50

Previously scattered in various papers and conference proceedings, the pertinent information compiled within this text, the first with such a presentation in a single volume, emphasizes the basic economic evaluation techniques as a means of comparing and selecting alternatives.

- 4. WATER RESOURCES ENGINEERING, Second Edition**

RAY K. LINSLEY and JOSEPH B. FRANZINI, both of Stanford University. *McGraw-Hill Series in Water Resources and Environmental Engineering*. 662 pages, \$17.50

Covering the full spectrum of water management, this edition contains new information on reference data, computer solutions, and added problems in metric units. Hydrologic concepts, legal aspects of water, open and closed channels, dams and spillways plus engineering economy are discussed.

- 5. WASTEWATER ENGINEERING:**

COLLECTION, TREATMENT, DISPOSAL. METCALF & EDDY, INC., Boston, Massachusetts. *McGraw-Hill Series in Water Resources and Environmental Engineering*. 768 pages (tent.), \$18.50 (tent.)

Logically organized and easily readable, this text offers an up-to-date treatment of wastewater engineering for the undergraduate student, the graduate student, and the practicing engineer. Principles and practices are presented in such a manner that the student will be able to apply the fundamentals to the solution of collection, treatment, and disposal problems.

- 6. GROUNDWATER RESOURCE EVALUATION**

WILLIAM C. WALTON, University of Minnesota. *McGraw-Hill Series in Water Resources and Environmental Engineering*. 672 pages, \$17.50

This ready reference book reflects the enormous progress that has been made in the groundwater resource evaluation field. Numerous illustrative case histories based on actual field data are provided.

- 7. THE ROLE OF WATER IN DEVELOPMENT**

A. WIENER, President, Tahal, Water Planning for Israel. *McGraw-Hill Series in Fluid Mechanics and Hydraulics*. 483 pages, \$14.50

The author's thesis is that the selection of the most appropriate development program depends upon the consideration of all relevant engineering, economic, social, and institutional aspects of the country involved.

-10 DAYS FREE EXAMINATION-

McGraw-Hill Book Company, Box 402, Hightstown, New Jersey 08520

Send me book(s) circled below for 10 days examination on approval. In 10 days I will remit for book(s) I keep, plus a few cents for postage and handling, and return unwanted book(s) postpaid. (We pay delivery costs if you remit with this coupon—same return privilege.) Include local sales tax if applicable.

1. 023900-2 2. 025590-3 3. 032263-5 4. 037959-9
5. 041675-3 6. 068051-5 7. 070150-4

NAME (print) _____

STREET ADDRESS _____

CITY _____ STATE _____ ZIP _____

For prices outside U.S., write McGraw-Hill, Int'l, N.Y.C. 10036

62EST272(sbn)

Circle No. 18 on Readers' Service Card

INDUSTRIAL WASTE PROBLEM ?



WHERE BUT IN A DESERT AT 13,000' MIGHT ONE FIND A BETTER PLACE TO DISPOSE OF INDUSTRIAL WASTE?

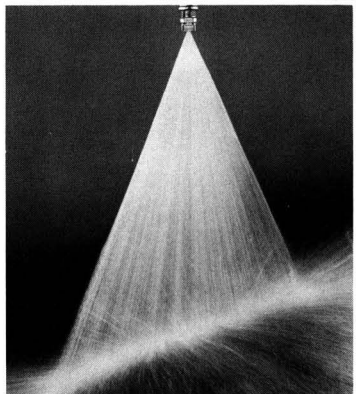
New Mexico Salt Water Disposal Company has in operation three wells which receive more than 30,000 barrels of oil field brine liquids daily. These wastes are dispersed into a natural porous formation nearly 3 miles below the earth's surface; a stratum known to contain more than 40 trillion barrels of pore space without shallow faulting and overlain by thousands of feet of protective aquatards. This system of liquid disposal meets every published standard. Other wastes can also be diluted into brine liquids for disposal; probably yours, too! Write or call for details.



New Mexico Salt Water Disposal Co. Inc.

Box 566, Roswell, N.M., 88201 (505) 622-1958

Circle No. 17 on Readers' Service Card



SPRAY NOZZLES

you name the need—we'll supply the nozzles!

Complete choice of capacities, spray angles and materials. All nozzle types... hollow and full cone, flat spray and air atomizing in choice of over 15,000 sizes and materials. Also spray guns and accessories. See your local representative or call us. Ask for 64 page Catalog 25A.

SPRAYING SYSTEMS CO.
North Ave. at Schmale Road, Wheaton, Ill. 60187
Telephone: 312 665-5000 / Telex No. 72-8409



PROMPT SHIPMENT FROM STOCK

Circle No. 8 on Readers' Service Card

Continuous System Models of Oxygen Depletion in a Eutrophic Reservoir

Louis P. Varga¹ and C. Paul Falls²

Department of Chemistry, Oklahoma State University, Stillwater, Okla. 74074

■ Several classes of mathematical simulation models have been tested in studies to relate the experimental dissolved oxygen (DO) concentrations to the parameters of eutrophication in Keystone Reservoir in north-central Oklahoma. One class of simulation model combined the features of mass transport by diffusion or turbulent transport, D , the measured flow rates in the impoundment, μ , and chemical reaction rates, r , in a series of special solutions to the equation

$$\dot{C} = D\nabla^2 C - \mu\nabla C \pm r$$

where C is the DO concentration and ∇ is the gradient. Based on the experimental DO levels in the reservoir, the transfer coefficients or overall reaction rate constants were determined for the reaction between dissolved organic matter and dissolved oxygen for both first- and second-order kinetics under both steady-state and time-dependent conditions, and in two space coordinates. These models compared favorably with deterministic compartment models with first-order kinetics in their ability to predict the assimilative capacity of a reservoir.

Keystone Reservoir is located on the Arkansas River in north-central Oklahoma with the dam 15 miles upstream from Tulsa at river mile 538.8. The dam was built by the U.S. Army Corps of Engineers for flood control, peak load hydroelectric power, recreation, and navigation purposes. Construction of the dam was completed in the fall of 1964, and the reservoir was filled to power pool level in April 1965. At the top of the power pool (elevation 723 MSL), the reservoir has a surface area of 26,300 acres, a gross storage capacity of 663,000 acre-feet, and 330 miles of shoreline. At flood stage (754 MSL), the maximum storage capacity is 1,879,000 acre-feet. Water can be released from the reservoir through the tainter or flood gates, the sluice gates, or the power penstocks which are 1.2, 20.1, and 21.5 m, respectively, below the power pool level.

The two chief tributaries to the reservoir are the Arkansas and Cimarron rivers, which converge about 2 miles above the dam to form the two main arms of the reservoir (Figure 1). The total drainage area is 74,500 square miles and extends from the Rocky Mountains in Colorado across southern Kansas and northern Oklahoma. The average volume of water flowing past Tulsa is about 4.5 million acre-feet per year (Dover et al., 1968).

The quality of the waters originating above Great Bend, Kan., on the Arkansas River and the Kansas-Oklahoma state line on the Cimarron River is, in general, good. However, from these points to Keystone Reservoir, numerous sources of natural brine, which originate from outcrops of halite, anhydrite, dolomite, and gypsum associated with evaporite deposits from Permian seabeds, occur. The waters of the two rivers are degraded by these natural pollutants to such an extent that they are unsuitable for general municipal, industrial, and agricultural use (Dover et al., 1968).

The Cimarron River flow averages only about one-fifth that of the Arkansas, but the Cimarron has four times the dissolved solids content of the Arkansas. Within the reservoir the dense Cimarron River water flows under the lighter water of the Arkansas and lateral tributaries. Chemical sampling on a grab-sample basis during a four-year period (Eley et al., 1967; Falls, 1969) indicated that the flow into the reservoir has a highly variable dissolved solids load. Large inflows following rains in the drainage basin may have a density different from water masses within the reservoir, and may flow for considerable distances through the reservoir without mixing. At times, the Cimarron arm of the reservoir contains a deep density current, which clearly is the salt-heavy Cimarron River inflow and which may be traced all the way to the dam. Diurnal variations in temperature imposed on the

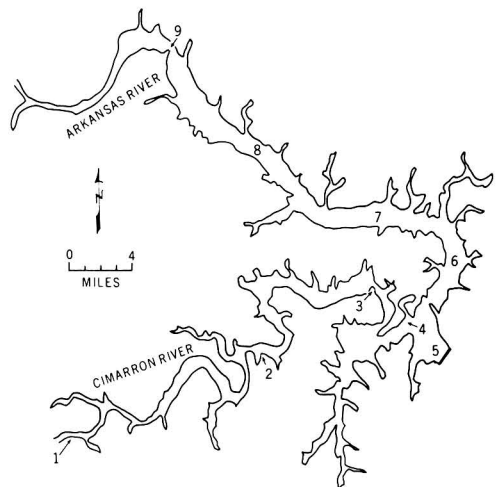


Figure 1. Keystone Reservoir, Okla., showing the location by number of sampling stations

¹ To whom correspondence should be addressed.

² Present address: Atlantic Richfield Co., Dallas, Tex. 75200.

river by changes in air temperature can be identified in the density current. During the summer, thermal stratification occurs in the deeper water near the dam, and its stability may be increased at times by water masses of high solids content.

Under these conditions, masses of water may be shut off from the atmosphere and become anoxic. One of the more obvious results of the complicated reservoir chemistry is that sulfates and organic matter are anaerobically converted to hydrogen sulfide and ammonia. Deep water masses were found which contained detectable sulfide and ammonium ion concentrations. Before these facts were recognized and steps taken to dilute the outflow from Keystone Reservoir, fish kills were noted below the dam caused by aeration and consequent rise in pH of the waters due to release of CO_2 and H_2S , followed by the formation of free ammonia from NH_4^+ . Core samples have shown that a black ooze presently covers the reservoir bottom; this contains iron sulfide, with significant concentrations of manganese, vanadium, and boron also present (Falls, 1969). The limnology of the reservoir is under intensive investigation and a considerable amount of data is available on plankton pigments (Spangler, 1968) and primary production (Eley, 1967).

Keystone Reservoir is a dynamic chemical system typical in many respects of most reservoirs in the Great Plains, but with the difference that the shoreline of Keystone is rapidly becoming urban. These studies and studies by Eley (1968) indicate that both natural and cultural eutrophication may be a problem in the future.

Eutrophication

The parameters of eutrophication most used by aquatic scientists are the standing crop of photosynthetic organisms (Strickland, 1960), the standing crop of zooplankton (Brooks, 1967), fish (Larkin, 1967), bottom fauna (Jonasson, 1967), attached algae, and rooted aquatic plants. Primary productivity is a major link in the total production of organic matter and is frequently used as a parameter of eutrophication.

In an oligotrophic lake, the oxygen is essentially uniform at all depths; in a typical eutrophic lake during the growing season, oxygen will be above or near saturation in the epilimnion, decrease through the metalimnion, and be depleted in the hypolimnion. This distribution is one of the major criteria Sawyer (1965) uses in classifying lakes. He is sure the lake is eutrophic when any portion becomes anaerobic.

Water in equilibrium with atmospheric oxygen has a well-defined redox potential (Morris and Stumm, 1967). At this potential, carbon, nitrogen, and sulfur exist in their highest oxidation states. Carbon should exist as CO_2 , HCO_3^- , or CO_3^{2-} ; nitrogen should be present as NO_3^- , and sulfur as SO_4^{2-} . Owing to the conversion of solar energy into chemical energy by photosynthetic processes, however, much of these elements exists in nature in their reduced state, mainly in organic compounds.

When the energy source is removed, for example, by the sinking of organic matter, the nonphotosynthetic processes tend to restore equilibrium through reaction of high-energy compounds. In a closed chemical system containing organic material—for example, carbohydrates—oxidation occurs first by reduction of dissolved oxygen. As the oxygen concentration decreases, the redox potential changes accordingly, resulting in the depletion of successively less easily reduced chemical species.

The rate of oxidative breakdown is dependent on the volume of organic matter available, generally the amount produced in the trophogenic zone. Hutchinson (1957) defines the lake as

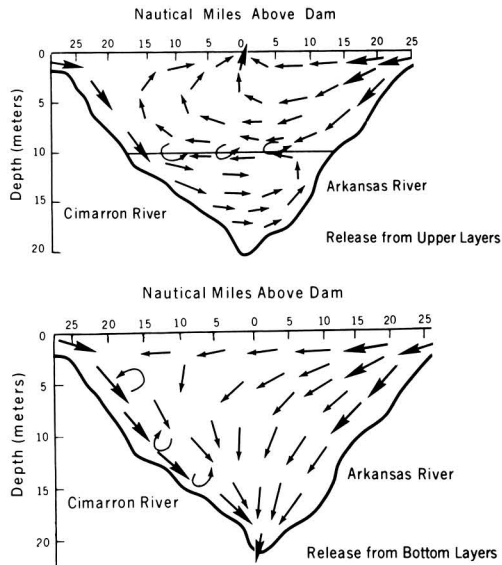


Figure 2. Hypothetical flow patterns in Keystone Reservoir

oligotrophic if the rate of oxygen depletion in the hypolimnion is between 0.004 and 0.033 mg/day/cm² and as eutrophic if between 0.05 and 0.14 mg/day/cm². Rates between these limits are considered representative of mesotrophic lakes.

The production or consumption of carbon dioxide by biological processes should vary inversely with that of oxygen. However, this is difficult to relate quantitatively to the biological activity since the distribution of carbon dioxide is dominated by the buffering effect of the carbonate system. Alkalinity and pH are widely used, however, to calculate or indicate its change.

Photosynthetic productivity according to some studies (Krauss, 1958), is directly related to the concentrations of phosphate and inorganic nitrogen nutrients in the trophogenic zone, as long as other factors remain favorable. At the time of the spring turnover, the abiotic component should be distributed almost equally at all depths while a major portion of the total phosphorus may be in particulate form (Eley, 1968).

Use of the amount of nutrients present and their distribution in natural water systems to follow the production of organic matter can be complicated. The uptake of nutrients by phytoplankton depends on the species; the nitrogen-to-phosphorus ratio; the turnover rate of nutrients; the nature of the nutrient sources; the presence of alga viruses (Safferman and Morris, 1964), toxins (Symons et al., 1964), and nutrients other than phosphorus and nitrogen (Goldman and Carter, 1965; Goldman, 1964); and a multitude of physical properties of the system. The most commonly measured chemical and physical properties related to the biological production of organic matter are dissolved oxygen, pH, alkalinity, orthophosphate, total phosphate, ammonia, nitrate, nitrite, organic nitrogen, organic carbon, light penetration, temperature, and total dissolved solids. In the present study, the dissolved oxygen concentration was chosen as the dependent variable. The simulation models thus attempted to predict this concentration as other reservoir parameters were varied so as to duplicate the experimentally measured DO concentration.

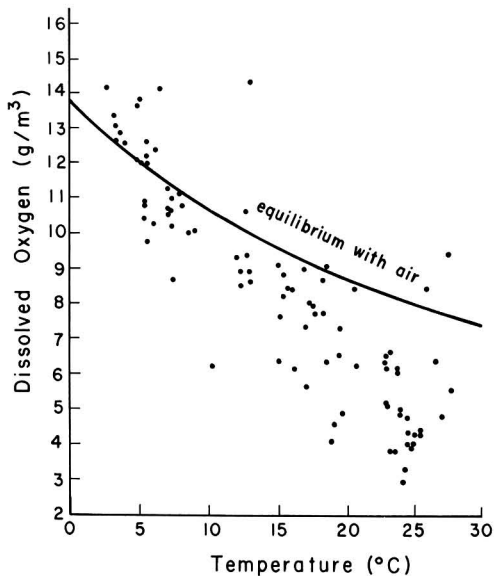


Figure 3. Measured oxygen concentrations in Keystone Reservoir as a function of temperature compared to the equilibrium saturation curve given by Truesdale (Truesdale et al., 1955)

Currents in Keystone Reservoir

Two distinct current patterns exist within the reservoir depending on whether water is released from the upper or the lower layers of the lake. A possible representation of these two currents is illustrated in Figure 2. When water is released from the upper layers, the dense Cimarron water flows along the bottom until it reaches the deepest part of the reservoir and then accumulates there. The less dense Arkansas River water distributes itself in the epilimnion and flows considerable distances up the Cimarron arm. A back flow, as illustrated in the figure, must occur to conserve mass. Frictional forces along the pycnocline would be expected to produce an inverse current in the hypolimnion.

When water is released from the bottom layers of the reservoir, the dense Cimarron water will flow along the bottom and out the dam. The less dense Arkansas water, which is about five times the Cimarron water in volume may exhibit its strongest movement in the lower half of the Arkansas arm, flowing toward the outlet gate. Smallest flows are expected in the upper layers. Some of the less dense water will flow up the Cimarron arm considerable distances before moving to the outlet.

These suggested flows are highly schematic and simplified, since there are many other forces which may come into play in addition to the density difference and forced convection. For example, the effect of winds will surely dominate the surface currents. The surface currents will probably be in the direction of the wind, while various types of countercurrents would be expected at intermediate depths.

Experimental

The DO concentration and other chemical and physical properties of the reservoir were observed periodically from May 1966 to May 1967, and monthly from May 1967 to June 1968. The locations of the sample stations are shown in Figure 1.

Until September 1967, all samples were taken by means of a G.M. Mfg. Co. 2-liter, clear plastic water sampler. The remaining samples were taken with a modified Kemmerer water bottle. The samples were stored in polypropylene or polyethylene bottles until analyzed.

Most of the methods used were similar in substance to those in APHA Standard Methods (1965), ASTM Manual on Industrial Waters (1965), and USGS Water-Supply Paper 1454 (Rainwater and Thatcher, 1960). After September 1967, DO concentrations were obtained in situ using a Precision Scientific galvanic-cell oxygen analyzer.

Figure 3 shows the average concentrations of oxygen at each station as a function of the average temperature. In the colder months, the values were near the saturation values, while during the warmer months, the values were well below saturation. The seasonal distribution of dissolved oxygen is shown in Figure 4. In the fall and winter, the oxygen was more or less uniformly distributed vertically; while in the spring and summer, its concentration was diminished in the bottom of the reservoir. These differences are commonly observed in reservoirs as the biological activity increases. This increased activity usually occurs when the solar radiation and temperature increase, and when the water column becomes more stable. The water along the bottom of the Cimarron River arm of the reservoir generally contained lower concentrations of dissolved oxygen than the overlying waters compared to that of the Arkansas arm. The greater vertical stability of the Cimarron waters, which prevented contact of the dense waters with the atmosphere, was a possible explanation of this observation.

Dynamic Reservoir Models

The theoretical expression for the concentration, C_i , of constituent i in a natural water system as a function of time and space coordinates in the absence of an electric field gradient or other unusual perturbation may be put in a form similar to that suggested by several workers (Morgan, 1967; Bowden, 1965; Berner, 1964; Richards et al., 1965; O'Connor, 1965):

$$\frac{\partial C_i}{\partial t} = D_i \left[\frac{\partial^2 C_i}{\partial X^2} + \frac{\partial^2 C_i}{\partial Y^2} + \frac{\partial^2 C_i}{\partial Z^2} \right] - \left[\mu_x \frac{\partial C_i}{\partial X} + \mu_y \frac{\partial C_i}{\partial Y} + \mu_z \frac{\partial C_i}{\partial Z} \right] + r_{i,n} \quad (1)$$

D_i is the diffusion or turbulent transport coefficient for constituent i , the μ 's are the solution velocity components in the X , Y , and Z directions, and $r_{i,n}$ denotes the rate of formation or disappearance of constituent i by process n in the neighborhood of the point (X, Y, Z) .

The approach used to develop a model describing the dissolved chemical species present in a reservoir ecosystem from the rather general Equation 1 was the adaptive one recommended by Bellman (1963). Initial models were idealized and somewhat crude, but flexible and open-ended so that new information could be incorporated and tested, and decisions made as to suitability.

Reduction to Ordinary Differential Equations and the Assumption of Steady State. If we assume the reservoir model to be a three-dimensional net with fixed boundaries similar to the compartmental models described by Watt (1968), the movement of constituent i through the mesh may be considered as the vector sum of the components of displacement in the X , Y , and Z directions summed over each mesh in the network. The X direction was taken as the direction of stream

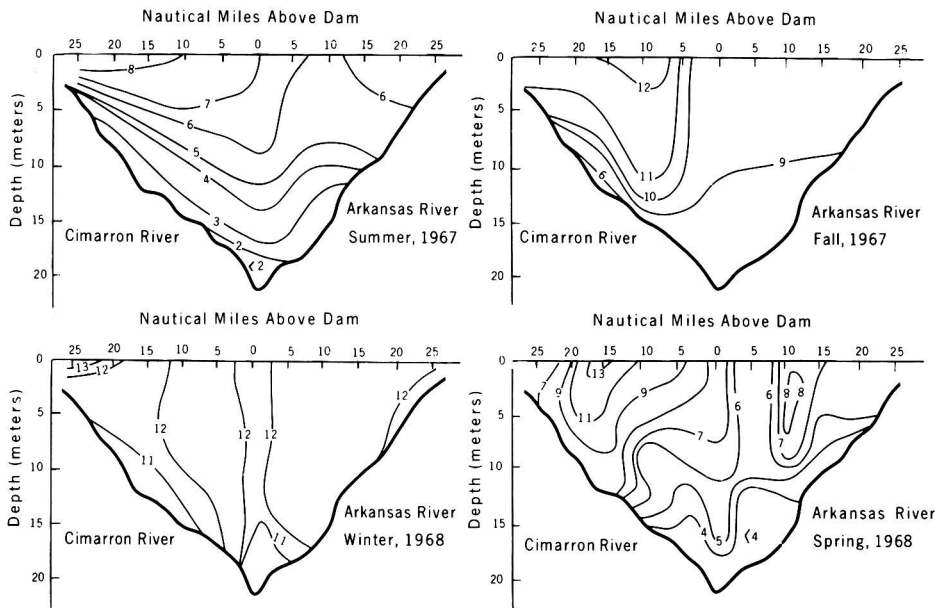


Figure 4. Seasonal distribution of dissolved oxygen concentrations (mg/l. or g/m³)

flow, the Y direction as the lateral direction across any arm of the reservoir, and the Z direction as depth. Then, certain initial assumptions were made for each coordinate which allowed an idealized solution for each component of displacement.

In the X direction, diffusion or turbulent transport was assumed to be negligible compared to the linear flow velocity. By setting the diffusion coefficient term equal to zero and considering only one constituent at a time, Equation 1 may be written

$$\frac{\partial C}{\partial t} = -\mu_x \frac{\partial C}{\partial X} + r \quad (2)$$

Under dynamic steady-state conditions, where the change of concentration with time of constituent i at any mesh point is zero, $\partial C/\partial t = 0$. Then Equation 2 becomes

$$\frac{dC}{dX} = \frac{r}{\mu_x} \quad (3)$$

From data (Eley et al., 1967; Falls, 1969; Cummings, 1965) corresponding to conditions along the Cimarron arm of Keystone Reservoir, several models were simulated based on different mechanisms of oxygen depletion.

OXYGEN DEPLETION IS A FIRST-ORDER FUNCTION OF THE DIRECTION VECTOR. The reaction between oxygen and dissolved organic matter (carbohydrate) may be represented by the simplified equation



If the rate of oxygen consumption at a point is proportional to the amount of organic matter present (forward rate constant is pseudo-first-order with respect to the concentration of dissolved organic), then

$$r = -k^*(org) \quad (5)$$

If the concentration of organic matter, in turn, is a function of depth in the reservoir, (org) = $0.04 \cdot Z$, and if the highly saline Cimarron River water is assumed to underflow the less dense waters of Keystone Reservoir in such manner that the depth, Z , is a constant fraction of the linear flow direction, $Z = 0.0005 \cdot X$, then

$$r = -k^*0.04 \cdot 0.0005 \cdot X \quad (6)$$

and the reservoir model becomes

$$\frac{dC}{dX} = -\frac{2 \cdot 10^{-5} \cdot k^* \cdot X}{\mu_x} \quad (7)$$

The linear flow velocity constant, μ_x , was 1500 m/day.

The solution of Equation 7 may be represented by

$$C = \int f(x)dx + IC \quad (8)$$

where $f(x)$ is the right-hand side of Equation 7. The initial condition value of C at $X = 0$, IC , was taken as 10 g/m^3 , and the integration interval was $5 \times 10^4 \text{ m}$, the approximate length of the reservoir arm. Figure 5 shows several solutions to Equation 8 for various values of k .

In the Y direction it was assumed that both diffusion or turbulent transport and advection were negligible compared to the linear flow velocity. Under the assumption of steady state, this resulted in elimination of terms in Equation 1 containing Y . For a typical riverine reservoir where impoundment is in a relatively narrow channel, this simplification appeared justified.

In the Z direction both diffusion or turbulent transport and convection were considered important as mechanisms for displacement of constituent i .

Equation 1 takes the form

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial Z^2} - \mu_z \frac{\partial C}{\partial Z} + r \quad (9)$$

where D_z is the diffusion or turbulent transport coefficient for constituent i in the Z direction and μ_z is the convection flow rate. Under the assumption of steady state in constituent i , the equation reduces to

$$\frac{d^2C}{dZ^2} = \frac{\mu_z}{D_z} \frac{dC}{dZ} - \frac{r}{D_z} \quad (10)$$

As outlined by Grodins (1963) the set of simultaneous equations which is the solution to Equation 10 for a given set of initial conditions, IC_1 and IC_2 , may be written

$$\begin{aligned} \text{Sum} &= \frac{\mu_z}{D_z} \frac{dC}{dZ} - \frac{r}{D_z} \\ \frac{dC}{dZ} &= \int \text{Sum} * dZ + IC_1 \\ C &= \int f_z(t) dZ + IC_2 \end{aligned} \quad (11)$$

where $f_z(t) = dC/dZ$. D_z was given the arbitrary but reasonable value of $8.6 \text{ m}^2/\text{day}$, and μ_z was 15 m/day . If the rate of oxygen depletion again is pseudo-first-order in organic concentration which, in turn, is a function of depth, as suggested above, then

$$r = -k * 0.04 * Z \quad (12)$$

where k is the forward reaction rate constant. Putting $IC_1 = 0$, $IC_2 = 10 \text{ g/m}^3$ and the integration interval at 25 m , the approximate depth of the reservoir at Keystone Dam, several solutions were found to Equation 10 for various values of k . The results are shown plotted in Figure 6.

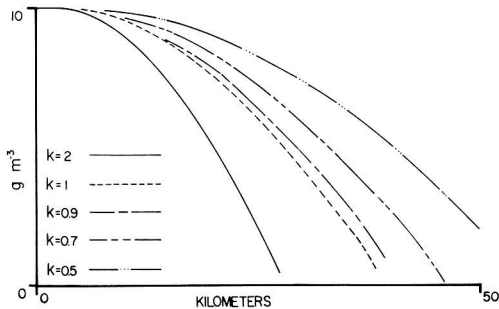


Figure 5. Oxygen concentration profiles along the reservoir bottom for various values of the first-order reaction rate constant, k (Equations 7 and 8)

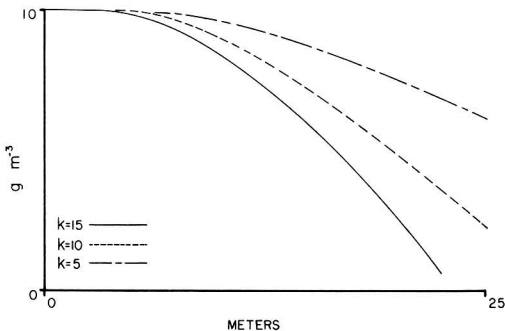


Figure 6. Oxygen concentration profiles as a function of reservoir depth for various values of the first-order reaction rate constant, k (Equations 10 and 11)

OXYGEN DEPLETION IS FIRST-ORDER WITH RESPECT TO THE CONCENTRATION OF DISSOLVED OXYGEN. If the dissolved organic concentration is constant throughout the reservoir (brought about, say, by constant inflow or by decay of organic matter) and the oxygen consumption rate in a reaction such as Equation 4 is pseudo-first-order with respect to the oxygen concentration, then the oxygen profile in a linear reservoir model corresponds to the exponential decay law. This trivial solution was not plotted, but the concept of first-order kinetics has been found useful in models incorporating compartments or mesh points discussed later.

OXYGEN DEPLETION IS SECOND-ORDER IN DISSOLVED ORGANIC AND OXYGEN CONCENTRATIONS. If a reaction such as Equation 4 obeys second-order kinetics such that

$$r = -k * (\text{org}) * C \quad (13)$$

and the organic concentration, again, is a function of reservoir depth, then application of Equations 8 and 11 yields dynamic reservoir models containing one fewer assumption than previous models. Putting

$$f_z(t) = - \frac{k * (\text{org}) * C}{\mu_z} \quad (14)$$

where $(\text{org}) = 0.04 * Z$, and $Z = 0.0005 * X$, several solutions to Equation 8 for the oxygen concentration along the reservoir bottom are shown plotted in Figure 7 by using the same initial conditions and integration interval as before.

Similarly, putting

$$r = -k * 0.04 * Z * C \quad (15)$$

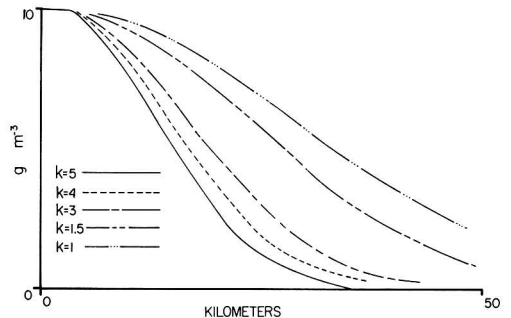


Figure 7. Oxygen concentration profiles along the reservoir bottom for various values of the reaction rate constant, k , assuming second-order kinetics (Equations 14 and 8)

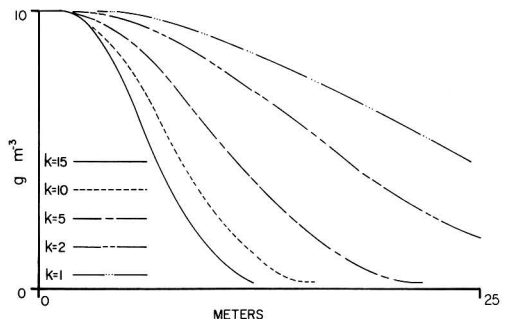


Figure 8. Oxygen concentration profiles as a function of reservoir depth for various values of the reaction rate constant, k , assuming second-order kinetics (Equations 15 and 11)

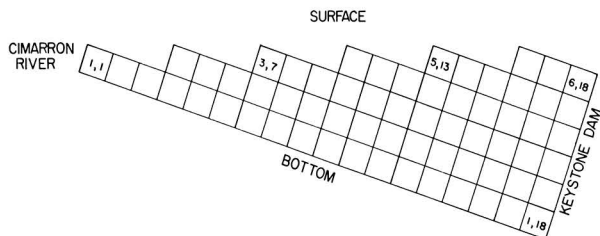


Figure 9. A two-dimensional reservoir model based on a 6×18 triangular matrix containing 63 elements

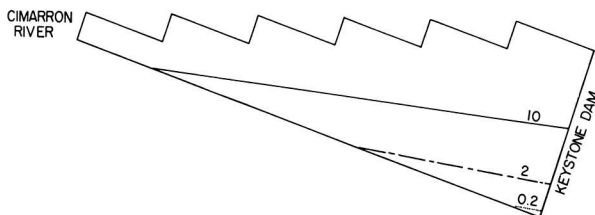


Figure 10. Oxygen concentration profiles (g/m^3) when the second-order rate constant, k , is $10 \text{ m}^3/\text{g}/\text{day}$

Equations 8, 11, 14, and 15 were applied to the reservoir model of Figure 9

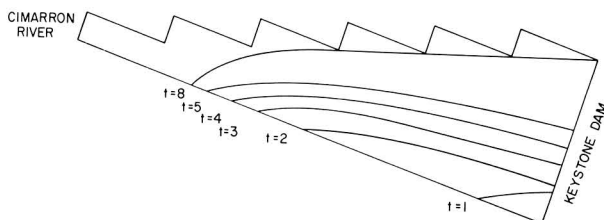


Figure 11. A time-dependent reservoir model

The profiles show the time in years required to produce given levels of water containing $2 \text{ g}/\text{m}^3$ of dissolved oxygen. Below each contour line the oxygen concentration would be less. The water mass originally was oxygen-saturated and the influx of dissolved organic matter was assumed exponential with a growth half-life of two years according to the conditions of secular equilibrium

several solutions to Equation 11 are shown plotted in Figure 8 for various values of k , by use of the same value as before for the other parameters.

A two-dimensional reservoir model may be constructed by alternate application of Equations 8 and 11 through a lattice or mesh incorporating the desired spatial characteristics. A basic reservoir network scheme which allowed efficient simulation of a stratified reservoir and was sufficiently flexible so that a triangular matrix of any dimension could easily be programmed is represented in Figure 9 by a 6×18 dimensioned form of the reservoir mesh. The matrix indices are shown for selected mesh points. The vector components of displacement were confined to the X and Z directions, thus simulating stream flow and allowing for the possibilities of diffusion, convection, density stratification, and other phenomena, but not allowing for lateral displacement. Basic FORTRAN algorithms for matrix manipulations when applied to the network in Figure 9 resulted in the oxygen concentration contours shown in Figure 10. Second-order kinetics were assumed for oxygen consumption (Equations 14 and 15 applied to Equations 8 and 11).

The FORTRAN code was imbedded in IBM's System/360 Continuous Systems Modeling Program (CSMP) (IBM, 1967). Specific changes in the program, particularly in the forcing functions of Equations 8 and 11 to allow for first- and second-order reactions, successive reactions, metabolic production of oxygen, effects of temperature and light on the process, etc., have given a broad base for mathematical experimentation.

A Time-Dependent Reservoir Model. A reservoir model in two space coordinates and one time coordinate was based on

Equations 3 and 10 where r is given by Equation 13. If we designate the original organic burden in the reservoir by G (such as may be obtained by brush and stumps in a virgin reservoir) and postulate an exponential growth of dissolved organic matter from the original organic burden in such a manner as to approach secular equilibrium, then

$$(\text{org}) = G*[1 - \exp(-0.693*t/2)] \quad (16)$$

assuming a growth half-life of two years. Under this assumption Equation 13 becomes

$$r = -k*C*G*[1 - \exp(-0.693*t/2)] \quad (17)$$

Putting this expression for r into Equations 3 and 10, solving by Equations 8 and 11, respectively, and programming the solutions through the reservoir mesh of Figure 9 for various increments of time yielded the results shown in Figure 11. Similarly the more realistic condition of transient equilibrium with respect to the organic burden of a virgin reservoir could easily be programmed.

A Branched Compartmental Material Balance Model. A 10-compartment model of the DO concentration ($\text{ppm} \cong \text{mg}/\text{l} \cong \text{g}/\text{m}^3$) in a reservoir ecosystem was based on the block diagram shown in Figure 12. If we follow the notation of Patten (1969), the X_n are the dynamic concentrations of dissolved oxygen in each compartment, and the $F_{i,j}$ are the mass transfer fluxes ($\text{g}/\text{m}^3/\text{day}$) in and out of each compartment, where i is the source and j is the destination; 0 refers to the external environment. The linear compartment dimension was 10^4 m per compartment. The fluxes, in turn, are products of flow rates or chemical reaction rates and the oxygen concen-

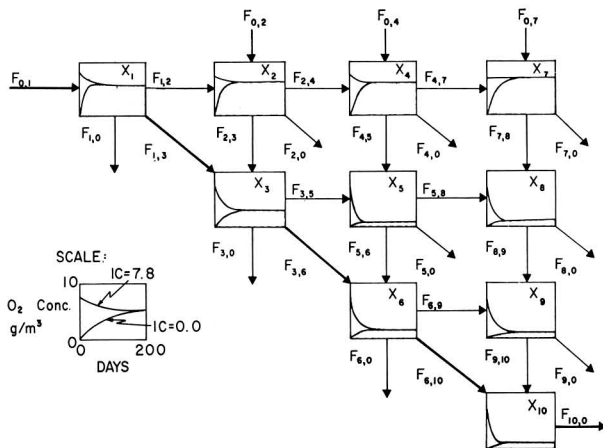


Figure 12. A branched 10-compartment reservoir model based on the set of DO mass balance differential equations given in Equation 18

Integration interval 0 to 200 days; initial conditions programmed at both 0.0 and 7.8 g/m³ of dissolved oxygen

tration in each compartment or each external source. Five rate constants were used in the model:

- $\mu_1 = 0.15$ compartment/day, the linear flow velocity constant
- $\mu_a = 0.05$ compartment/day, the advection flow rate
- $\mu_c = 0.005$ compartment/day, the convection flow rate
- $k_a = 0.0024$ compartment/day, the aeration specific rate constant (Downing and Truesdale, 1955)
- $k = 0.10 \text{ day}^{-1}$, the first-order reaction rate constant

DO input was programmed in terms of the yearly average Cimarron River flow rate times the saturation concentration of oxygen in moderately saline water (Truesdale et al., 1955) ($F_{0,1}$ shown below), and the given value for the aeration specific rate constant, k_a , at the reservoir surface. The value of $F_{10,0}$ included the only oxygen loss from the reservoir due to normal flow discharge, while other losses were taken as first-order oxygen depletion due to the overall BOD and COD. The pertinent relations are as follows (in g/m³/day per compartment):

Oxygen input	Density, stratified flow	Advective flow
$F_{0,1} = \mu_1 * 7.8$	$F_{1,3} = \mu_1 * X_1$	$F_{1,2} = \mu_c * X_1$
$F_{0,2} = k_a * 286$	$F_{3,6} = \mu_1 * X_3$	$F_{2,4} = \mu_c * X_2$
$F_{0,4} = k_a * 286$	$F_{6,10} = \mu_1 * X_6$	$F_{3,5} = \mu_c * X_3$
$F_{0,7} = k_a * 286$	$F_{10,0} = (\mu_1 + k) * X_{10}$	$F_{4,7} = \mu_c * X_4$
		$F_{5,8} = \mu_c * X_5$
		$F_{6,9} = \mu_c * X_6$

Oxygen depletion flux	Convective flow
$F_{1,0} = k * X_1$	$F_{2,3} = \mu_c * X_2$
$F_{2,0} = k * X_2$	$F_{4,5} = \mu_c * X_4$
$F_{3,0} = k * X_3$	$F_{5,6} = \mu_c * X_5$
$F_{4,0} = k * X_4$	$F_{7,8} = \mu_c * X_7$
$F_{5,0} = k * X_5$	$F_{8,9} = \mu_c * X_8$
$F_{6,0} = k * X_6$	$F_{9,10} = \mu_c * X_9$
$F_{7,0} = k * X_7$	
$F_{8,0} = k * X_8$	
$F_{9,0} = k * X_9$	

The set of mass balance differential equations describing the time rate of change of concentration, then, is based on the difference between input and loss in a manner similar to that described in the DO model given by Pence and co-workers (Pence et al., 1968):

$$\begin{aligned} \frac{dX_1}{dt} &= F_{0,1} - (F_{1,2} + F_{1,3} + F_{1,0}) \\ \frac{dX_2}{dt} &= F_{1,2} + F_{0,2} - (F_{2,3} + F_{2,4} + F_{2,0}) \end{aligned} \quad (18)$$

$$\frac{dX_3}{dt} = F_{1,3} + F_{2,3} - (F_{3,5} + F_{3,6} + F_{3,0})$$

$$\frac{dX_4}{dt} = F_{2,4} + F_{0,4} - (F_{4,7} + F_{4,5} + F_{4,0})$$

$$\frac{dX_5}{dt} = F_{3,5} + F_{4,5} - (F_{5,8} + F_{5,6} + F_{5,0})$$

$$\frac{dX_6}{dt} = F_{3,6} + F_{5,6} - (F_{6,9} + F_{6,10} + F_{6,0})$$

$$\frac{dX_7}{dt} = F_{4,7} + F_{0,7} - (F_{7,8} + F_{7,0})$$

$$\frac{dX_8}{dt} = F_{5,8} + F_{7,8} - (F_{8,9} + F_{8,0})$$

$$\frac{dX_9}{dt} = F_{6,9} + F_{8,9} - (F_{9,10} + F_{9,0})$$

$$\frac{dX_{10}}{dt} = F_{6,10} + F_{9,10} - F_{10,0}$$

The results, starting both with an oxygen-empty reservoir (simulating an ecological disaster) and an oxygen-saturated reservoir, are depicted in Figure 12. IBM's System/360 CSMF numerical integration function (IBM, 1967) was used to solve these equations over the integration interval of 0 to 200 days.

Conclusion

Taking the lowest measured oxygen concentration value of 2 g/m³ given in Figure 4 (summer, 1967) as a convenient criterion of incipient eutrophication, comparison of this real condition of Keystone Reservoir with various parameters used to construct the several models are shown in Table I.

From Hutchinson's (1957) definition of the eutrophic condition in a natural water system as that in which the oxygen depletion flux is 0.05 mg/day/cm² (0.5 g/day/m²) or higher, and assuming that this depletion flux eventually brings about the anoxic condition, we may consider all the values in the column in Table I labeled "Value to give $\leq 2 \text{ g/m}^3$ " as the critical parameters leading to eutrophication in each particular model.

It should be noted, of course, that several of the reservoir model configurations of Table I are related. For instance, the models corresponding to Figures 5-8 are basic to the construction of the models depicted in Figures 10 and 11. These relations show promise for future modeling studies, but the

Table I. A Summary of Model Configurations and the Critical Values of the Reaction Rate Constant, k , Which Led to Eutrophication in Each Model

Figure	Reservoir model configuration	Forward reaction rate constant, k	
		Type	Value to give $\leq 2 \text{ g/m}^3$
5	Linear (along reservoir bottom)	First-order in dissolved organic; (org) = $f(Z)$	0.5 day^{-1}
6	Depth axis	Same as above	10.0 day^{-1}
7	Linear (along reservoir bottom)	Second-order in dissolved oxygen and organic	$1.0 \text{ m}^3\text{g}^{-1}\text{day}^{-1}$
8	Depth axis	Same as above	$2.0 \text{ m}^3\text{g}^{-1}\text{day}^{-1}$
10	6×18 Triangular matrix	Second-order in dissolved oxygen and organic	$10.0 \text{ m}^3\text{g}^{-1}\text{day}^{-1}$
11	6×18 Triangular matrix	Approach to secular equilibrium in dissolved organic	$70.0 \text{ m}^3\text{g}^{-1}\text{day}^{-1}$
12	Branched 10-compartment model	First-order in dissolved oxygen	0.1 day^{-1}

branched compartment model shown in Figure 12 appears to be the most powerful tool in reservoir ecosystem modeling. Not only can the input and output fluxes of any given constituent be monitored at each compartment in the reservoir network, but the effect of each flow rate and chemical reaction rate on the critical fluxes and concentrations can be readily followed and interpreted. Direct readout of the oxygen depletion flux from the hypolimnetic compartment X_3 , for instance, indicated a value of 0.32 g/day/m^2 , approaching Hutchinson's range for a mesotrophic system (Hutchinson, 1957). A value of 0.6 g/day/m^2 was obtained for the epilimnetic compartment X_4 , suggesting a eutrophic system. The rate of recovery from an initial condition of zero dissolved oxygen and the oxygen depletion rate starting with an oxygen-saturated system as depicted in Figure 12 are direct simulations of the assimilative capacity of a reservoir.

All the models used have duplicated some aspect of the high oxygen loss encountered in Keystone Reservoir, and the results presently are being used in time-dependent studies of compartment models with nonlinear transfer coefficients.

CSMP program listings are available on request.

Acknowledgment

We wish to thank K. A. Kocksiek for some of the oxygen analyses referred to in this paper.

Literature Cited

- American Public Health Association, "Standard Methods for the Examination of Water and Wastewater," 12th ed., APHA, New York, N.Y., 1965.
 American Society for Testing Materials, "Manual on Industrial Water and Industrial Waste Water," ASTM, Philadelphia, Pa., 1965.

- Bellman, R., Ed., "Mathematical Optimization Techniques," University of California Press, Berkeley, Calif., 1963, pp 333-9.
 Berner, R. A., *Geochim. Cosmochim. Acta* **28**, 1497 (1964).
 Bowden, K. F., in "Chemical Oceanography," J. P. Riley, G. Skirrow, Eds., Academic Press, New York, N.Y., 1965, pp 43-120.
 Brooks, J. L., *Water Sewage Works* **114**, 490 (1967).
 Cummings, T. R., "Chemical Character of Surface Waters of Oklahoma, 1961-62," Bull. No. 24, Oklahoma Water Resources Board, 1965.
 Dover, T. B., Leonard, A. R., Laine, L. L., U.S. Geol. Survey Water Supply Paper 1890 (1968).
 Downing, A. L., Truesdale, G. A., *J. Appl. Chem.* **5**, 570 (1955).
 Eley, R. L., MS Thesis, Oklahoma State University, 1967.
 Eley, R. L., Department of Biology, Southern State College, Magnolia, Ark., personal communications, 1968.
 Eley, R. L., Carter, N. E., Dorris, T. C., Proceedings of the Reservoir Fishery Resources Symposium, Athens, Ga., 1967, pp 333-357.
 Falls, C. P., PhD Thesis, Oklahoma State University, 1969.
 Goldman, C. R., *Verh. Int. Verein. Limnol.* **15**, 365 (1964).
 Goldman, C. R., Carter, R. C., *J. Water Pollut. Contr. Fed.* **37**, 1044 (1965).
 Grodins, F. S., "Control Theory and Biological Systems," Columbia University Press, New York, N.Y., 1963, pp 27-44.
 Hutchinson, G. E., "A Treatise on Limnology, Vol I, Geography, Physics, and Chemistry," Wiley, New York, N.Y., 1957, p 644.
 IBM Applications Program H20-0367-1 System/360 Continuous System Modeling Program (360A-CX-16X), User's Manual, 1967.
 Jonasson, P. M., *Water Sewage Works*, **114**, 490 (1967).
 Krauss, R. W., *Ann. Rev. Plant Physiol.* **9**, 207 (1958).
 Larkin, P., *Water Sewage Works* **114**, 490 (1967).
 Morgan, J. J., *Adv. Chem. Ser.* **67**, 1-29 (1967).
 Morris, J. C., Stumm, W., *ibid.*, 270 (1967).
 O'Connor, R. J., *Proc. Amer. Soc. Civil Eng.* **91**, SA1, 23 (1965).
 Patten, B. C. (of the Department of Zoology, University of Georgia, Athens), seminar presented to the Department of Zoology, Oklahoma State University, May 1969.
 Pence, G. D., Jr., Jeglic, J. M., Thomaan, R. V., *Proc. Amer. Soc. Civil Eng.* **94**, SA2, 381 (1968).
 Rainwater, F. H., Thatcher, L. L., U.S. Geol. Survey Water Supply Paper 1454 (1960).
 Richards, F. A., Cline, J. D., Broenkow, W. W., Atkinson, L. P., "Some Consequences of the Decomposition of Organic Matter in Lake Nitinat, an Anoxic Fjord," Office of Naval Research Contract NONR 477 (37), Project NR083-012, 1965.
 Safferman, R. S., Morris, M. E., *J. Amer. Water Works Ass.* **56**, 1217 (1964).
 Sawyer, C. N., USPHS Publication No. 999-WP-30, 215 (1965).
 Spangler, F., PhD Thesis, Oklahoma State University, 1968.
 Strickland, J. D. H., *Bull. Fish. Res. Bd. Can.* **122**, 1 (1960).
 Symons, J. M., Weibel, S. R., Robeck, G. G., USPHS Publication No. 999-WP-18 (1964).
 Truesdale, G. A., Downing, A. L., Lowden, G. F., *J. Appl. Chem.* **5**, 53 (1955).
 Watt, K. E. F., "Ecology and Resource Management," McGraw-Hill, New York, N. Y., 1968, pp 252-73.

Received for review August 7, 1969. Resubmitted September 29, 1970. Accepted June 21, 1971. Presented at the 159th National ACS Meeting, Houston, Tex., Feb. 22-27, 1970. This work was supported, in part, by the Oklahoma State University Research Foundation, the University Computer Center, the Oklahoma Oil Refiners Council, and the Federal Water Pollution Control Administration (now EPA). Continuing studies supported by the Atomic Energy Commission, Contract No. AT-(11-1)-2070.

Formation and Degradation of Aerocolloids by Ultraviolet Radiation

Alexander Goetz¹ and Olgierd J. Klejnot

Atmospheric Research Group, Altadena, Calif. 91001

■ Formation of aerocolloids from traces of hydrocarbons in air occurs in a steady airflow exposed for 6–60 sec to the light of quartz ultraviolet lamps, which generates ozone oxidant. The same oxidant forms aerocolloid in darkness with such reactive hydrocarbons as turpentine and cyclohexene. Enhancing factors are: ultraviolet light, humidity, nucleating matter, and ammonia. The yields are reduced on adding ammonia in the dark and on shifting the humidity by mixing of airstreams. Degradation of airborne aerocolloid by ozone with short-wavelength uv light is observed, after a peak of formation, at lower humidities of $\leq 50\%$ rh. The ultraviolet degradability of impactor deposits depends on formation conditions and nature of the hydrocarbon.

The finding that aerocolloids are formed in flows of atmospheric air exposed to ultraviolet light for 6–60 sec has led us to the development of a new instrument, the ultraviolet cascade, useful in studying the phenomenon, tracing natural hydrocarbon patterns, and detecting contaminants in the atmosphere (Goetz and Klejnot, 1967).

This paper deals with the effects of flow rate, exposure, and humidity on the yields of oxidant and aerocolloid. Also, the effects of nucleating matter, ammonia, structure of hydrocarbons, and humidity shift are discussed.

Procedure

Air Control. For laboratory studies, air from a compressed-air system was subjected to molecular filtration, after which no condensation nuclei were found with an Aitken counter. Ultraviolet irradiation of this air gave no indication with a Royco aerosol photometer, but the nuclei count became too high to measure.

The air was released at 5 psia and passed through a charcoal trap (metal can), a set of molecular membranes, a valve with flowmeter, F_1 , and the humidity control assembly, to the ultraviolet cascade (Figure 1). A small branch flow in the hydrocarbon diluter (F_2 – F_5 , U , X) was charged with saturated vapor of hydrocarbon. An excess of the air over the suction of the moving-slide impactor (MSI) and the Royco photometer (R) was blown off at Z .

For field studies, ambient air was sucked in through the humidifier and ultraviolet cascade by the sensor device (MSI or Royco), and the bypass (Z) was closed. The exposures were determined by the branching of the flow. A Hypercon flowmeter (by Goetz) was used to measure the suction by a compensation method, which avoids flow restrictions. The MSI and the sampling of natural aerocolloids are described in detail elsewhere (Goetz, 1969).

Humidity Control. The sampled airstream passed through the humidity control assembly, consisting of dry and wet tubes, heating pads, and a mixing valve.

Four horizontal tubes were stacked in pairs, the empty dry ones atop the wet tubes. The latter were lined with filter paper that soaked up distilled water standing at the bottom. The filter paper was impregnated with silver hydroxide to make it permanently antiseptic without inducing any gas traces into the airstream. Heating pads on the wet tubes could be switched off or operated at a low or high rate of heating. Thus, at high flow rates, any required humidities could be maintained by compensating for evaporative cooling. The mixing valve assured a continuous adjustment of humidity by mixing original air and humidified air in any desired ratio. A slide superimposed two pairs of round openings of $\frac{1}{2}$ in. diameter each, opening equal half areas in the center position, shifting either way off-center, and closing the one or the other passage in each extreme position while maintaining a constant total opening. The adjusted air mixture passed a hygrometer, placed in an airtight box with window and slide valve, which permitted bypassing the hygrometer box during impaction of aerocolloids.

Additives Control. Reactants like hydrocarbons, ammonia, and sulfur dioxide were added after humidification, to avoid their absorption and subsequent desorption in the humidifier tube. In the HC diluter (Figure 1) with the two dilution stages, X and Y , and charging trap U (test tube 300×30 mm), a small branch flow was saturated with HC vapors at room temperature. Part of the mixture was wasted at F_5 . Gases were introduced directly through flowmeter F_3 . The gaseous reagents—methane, acetylene, ethylene, *trans*-butene-2—were CP-grade chemicals in lecture bottles (Matheson). Propane was a commercial mixture of propane and butane (liquid gas). All liquid HC samples were of reagent grade (Matheson, Eastman, Baker).

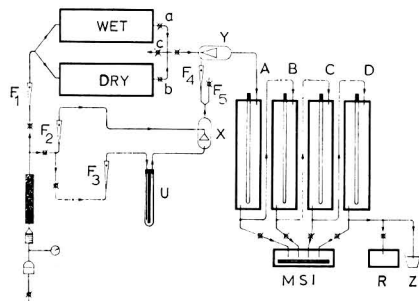


Figure 1. Flow pattern of humidifier, hydrocarbon diluter, ultraviolet irradiation cascade, and sensors

Humidifier chambers (wet, dry); humidifier mixing valve a , b ; bypass to impactor c ; diluter flowmeters F_2 , F_3 , F_4 ; hydrocarbon charger U ; bleeder cock F_5 ; mixing stages X , Y ; ultraviolet cascade stages A , B , C , D ; moving-slide impactor MSI ; Royco aerosol photometer R ; main flowmeter F_1 ; bypass Z

¹ Deceased, January 12, 1970.

² Present address: 3024 Zane Grey Terrace, Altadena, Calif. 91001.

Ammonia was added by passing the main airstream over a small cylindrical dish (14 mm i.d., 8 mm deep, 1.5 cm² surface) with ammonia solution, that was placed in a glass chamber with bypass by a three-way cock. The solutions were dilutions of concentrated NH₃ (25%) in ratios of 1/50, 1/100, and 1/500. The ammonia concentrations produced in the air passing the evaporation chamber were estimated by visual comparison of test tubes containing Nessler's reagent with standard quantities of ammonia, and Nessler's reagent through which 20 or 60 liters of the air were bubbled at 2 l./min. The following results were obtained:

Dilution	Rh%	Ppm NH ₃ in air
1/50	80	11.0
1/50	20	2.60
1/100	80	1.69
1/100	22	0.66

At 0.66 ppm NH₃, 20 liters of air carry 0.01 mg of NH₃. Apparently, more ammonia evaporates into the humid air than into the dry air.

The Ultraviolet Cascade. The present method of ultraviolet irradiation treats a steady flow of the air sample in a "cascade" of 1-liter cylinders, fitted with mercury arcs of quartz glass (PCQ 90-1, Ultra-Violet Products, Inc., San Gabriel, Calif., 34 cm long, 8 mm o.d.). The four cylinders mounted vertically in a water tank, an oscillating-type water pump, high voltage transformers, humidifier, hygrometer, and control panel are contained in a portable rack. The four cylinders (chromium-plated and polished inside) are connected in series and fractional flows may be withdrawn after each cylinder (irradiation stage). In the front view of Figure 2, the ultraviolet lamps are on the right in their water tank. On the left are the humidifier with hygrometer and switchboard for the lamp transformers, water pump, and humidifier heating tape. At upper left are the transformer switches for various lamp arrangements.

Flows and Exposure Time. The ultraviolet cascade renders identical, optimal flow conditions in each stage. The sampled airflow enters tangentially topside and leaves centrally at the bottom. The rotary flow centers the oxidant layer formed near the lamp surface and effects a mixing of hydrocarbon and

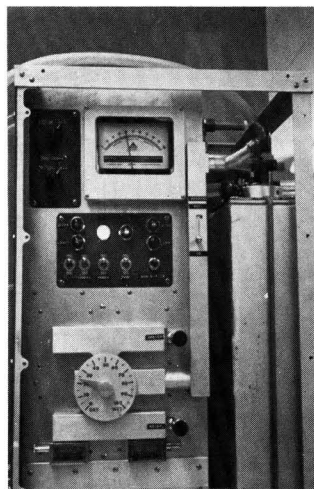


Figure 2. Ultraviolet cascade, front view

oxidant where the energetic fraction of the light is available (Figure 3). The constant total flow F_T was usually adjusted to exceed slightly the suction requirements of the four-slit *MSI* and Royco photometer (note bubbler Z, Figure 1). It is necessary to keep the conditions constant for several minutes before an impaction, to avoid drifting of the formation of aerocolloid. As the fractional flows are equal, their light exposure in each stage increases in a nearly exponential series. The mean exposure can be varied between a few seconds and 1 min by the flow rate, number of stages, and flow branching. Longer exposures (120–240 sec) are obtained with a constant flow through the stages or by adding more stages. The exposure time follows from $t = V/F$ in minutes when stage volume V is 1 liter and F is given in l./min, or in seconds from $t = 60/F$ under the same conditions.

Temperature Control. The temperature was held at about 27°C by circulating the water of the water jacket and an external volume of equal size.

Aerocolloid Evaluation. The evaluation of the aerocolloid concentration at each stage of the ultraviolet cascade was done with an aerosol photometer, the intake of which was shifted from stage to stage, and by microscope photometry of deposits impacted from selected stages in the moving-slide impactor (Goetz, 1969). Both methods depend on light-scattering by particles of the size 0.1–1.0 μm, called S_R and S (S_R obtained with the Royco instrument). The units of S are arbitrary, self-consistent units obtained from readings of a five-decade microamperemeter (divided by 10²) and standardized to a certain albedo S of a certain ground glass standard slide by balancing the photocell, microscope, and objective (Ultrapak 6.5 Leitz-Wetzlar) against the lighting system. The low-angle darkfield technique applied measures light scattered at a 90° angle, whose intensity depends on the adjustment of the light source (Goetz, 1969).

The Royco aerosol photometer Model 230 was equipped with an intake gas cock and with a bypass cock to the pump. This avoided the usual rotary port with rubber rings, and gave two settings for the intake suction at 1 or 2 l./min.

The moving-slide impactor (*MSI*) employed as the main

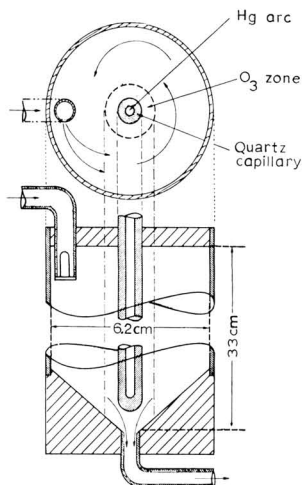


Figure 3. Schematic vertical cut through the irradiation stage unit. The airflow rotates (arrows) around the central quartz tube and leaves at center of the unit's lower end

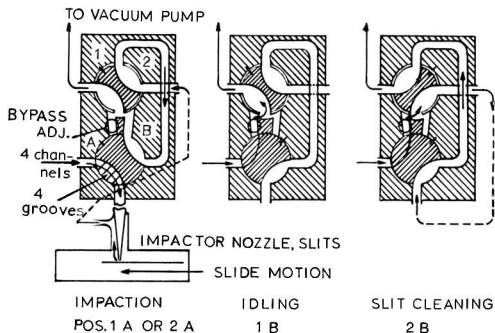


Figure 4. Flow alternator: flow sheet in front view

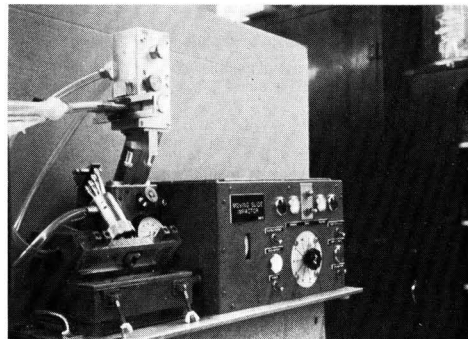


Figure 5. Flow alternator and moving-slide impactor

evaluation device is a single-stage impactor with four equal slits arranged in one line. The slide is moved across the line of slits at a constant speed, or in a step sequence of constant speeds (Goetz, 1969).

During a single pass, the collecting surface of a metallized microscope slide receives simultaneously four parallel ribbons of aerocolloid deposits. A synchronous drive allows a variation of speeds in 10 doubling steps from 2^0 to 2^9 . Thus, it is possible to vary the deposit density up to 512-fold. Up to 10 such steps can be evaluated in one slide length with a microphotometer or by microscopic counting. A limiting high-deposit density is usually attained, at which coalescence of the particles occurs and the counts, as well as the light-scattering, sharply fall off.

The impactor has a bypass system in order to keep the flow in the ultraviolet cascade constant before, during, and after an impaction (flow alternator, Figure 4). The reported S data refer to deposits obtained with a pressure drop of $\Delta p = 90$ mm Hg at the slit orifice.

The flow alternator is an aluminum block (2024 ST4 Alum.) with two bores housing two cocks held in place by a front plate. Each bore has five outlets to make possible the three functions: impaction, idling (bypass), and slit cleaning (reverse flow). One internal duct, one external Tygon connection between impactor head and flow alternator, and two short bores between the cocks provide the necessary channels (Figure 4). The cocks are closely fitted and lubricated with stopcock grease of a vacuum grade (rubber base, not silicone or apiezone which tend to flow).

The moving-slide impactor with alternator is shown in Figure 5. The instrument is opened for slide access. Deposits of the *MSI* are concentrated in a small area, and their aging, desiccation, and degradation by ultraviolet light can be evaluated by measuring repeatedly their light-scattering S . Aging of deposits required weeks of storage for completion. Rapid aging was accomplished by heating in a vacuum oven for several hours at 100°C . Desiccation was achieved by storing the slides in an evacuated desiccator containing a dish with powdery phosphorus pentoxide.

For degradation by ultraviolet irradiation, one of the 34-cm ultraviolet lamps was mounted horizontally above the slides laid out side by side, with a 2-in. vertical separation to the lamp. Exposures used were 30 min, 1, 2, 8, 16 hr, or sequences in ratios 1:3:10 for logarithmic irradiation equivalents.

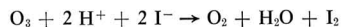
Oxidant Measurements. For the determination of oxidant, an irradiated airstream of 2 l./min was passed under positive pressure through a bubbler (intensive washer with deflecting plate) and a flowmeter. Larger flows were divided with a tee

and bypass. The air samples were 5 or 10 liters. The bubbler contained 10 cc of an acidic (0.4*N*) 2% KI solution, freshly mixed for each test from 40 cc of 5% KI solution, 40 cc of distilled water, and 20 cc of 2*N* H_2SO_4 . Neutral stock solution of KI, which, over a few weeks, acquired the yellow of free iodine, was decolorized by a 10-min exposure over coconut charcoal and filtration. Iodine liberated by the oxidant was titrated with a 0.02*N* standard thiosulfate solution with an end point indication with starch. For a 10-liter air sample, 1 ml of 0.02*N* thiosulfate solution equals 12.25 ppm oxidant. For a study of the influence of F , t , and relative humidity on the oxidant level, two connected ultraviolet cascades with eight consecutive stages were used. For constant voltage, all eight lamps were on, while one outlet was connected to the bubbler.

Dark-Reaction Tests. In the dark-reaction tests, a tee at the inlet of stage *C* was used to add the hydrocarbon-air. Deposits were made from both dark stages, *C* and *D*. The flows in *AB-CD* were 3.0, 3.0, 6.0, 3.5 l./min, the exposures were 20, 20, 10, 17 sec, respectively. The HC-air containing 5.0 ppm of turpentine, before mixing with the oxidant stream, was diluted to 2.5 ppm in the combined stream (3 l./min each stream). For arranging different humidities in the two streams, both the main flow F_1 and that of the humidifier were branched and mixed, with one additional flowmeter and difference reading of flowmeter f_i . For $\text{rh} < 18\%$, a silica gel tower was put between pressure regulator and Millipore filter unit. Ammonia effects were studied at about 5 ppm NH_3 from a 1/50 dilution.

Results and Discussion

Production and Decay of Oxidant. Oxidant is detected immediately on irradiation of air with quartz mercury arcs. The attained ozone concentrations depend on exposure, humidity, and flow rate besides the flow geometry (Figure 3). Ozone oxidant was measured by iodometry in acidic solution:

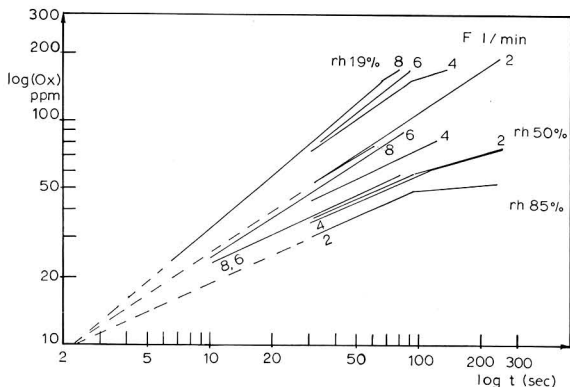


The plot of ozone concentrations vs. exposure suggests that under all conditions of flow and humidity a concentration of 10 ppm is reached in 1.2 to 2.3 sec. The ozone concentration rises steeply at longer exposures (10–100 sec), and it rises also with the flow rate F and with decreasing relative humidity (Figure 6). A decay of the oxidant in the darkened cascade (3 dark stages, *BCD*) was observed only at high humidity and was marked by lower titration values.

Ultraviolet lamps shielded with Vycor-7910 produced no

Figure 6. Oxidant formation at total exposure t , depending on flow F and relative humidity

The curves converge below 10 ppm and 2.3 sec



oxidant, but their light accelerated the decay of oxidant at both high and low humidity.

The oxidant concentration was strongly reduced by added low concentrations of ammonia. Reduction of the oxidant by hydrocarbon was verified with toluene, and formation of aerocolloid occurred only in presence of oxidant.

Formation and Degradation of Aerocolloid

Ultraviolet Reaction with Toluene. Toluene, which is moderately reactive, was used in studies of the formation of aerocolloid in the ultraviolet cascade. Conditions other than the variable under study were held constant. The impactor deposits were soluble in water (yellow).

Aerocolloid yields obtained as light-scattering levels S_R (airborne) or S (impacted) depend among other factors on the exposure t . Within the ultraviolet cascade, a rise (formation) is followed by a fall (degradation). This was shown in three ways: measuring S_R at the first stage A for various flows $F = 3-16$ l./min; measuring S of deposits taken at one flow rate from each of the four stages $ABCD$ (Figure 7); measuring S of deposits taken simultaneously from the four stages $ABCD$, which had, therefore, four different flows and exposures. Compared to the second method, equal exposures gave unequal yields, depending on the flow rate F (Figure 7). The top yields were observed at $F = 4$ l./min; at flows of 3-2 l./min the yields were somewhat smaller and at larger flows they fell off more strongly.

The third method of simultaneous four-track deposition was the most used for its convenience.

It was found, by all three methods, that a rapid initial formation of aerocolloid peaks at a time t_{max} (6-60 sec) after which S declines linearly in $\log S$ vs. t . This is modified by the flow rate, concentration and nature of hydrocarbon, and humidity. Low humidity favors the degradation, whereas high humidity favors the formation of aerocolloid.

Nucleating matter promotes the production of aerocolloid (Goetz and Pueschel, 1965). In the Haagen-Smit reaction (Haagen-Smit, 1952; Haagen-Smit et al., 1953, 1956) photochemical oxidation of hydrocarbon traces by visible light in presence of nitrogen oxides occurs. Only in the absence or deficiency of nucleating matter will autonucleation occur, with formation of relatively unstable new particles and a decrease in the quantum yield of the light (Goetz and Pueschel, 1967).

This effect of nucleating matter was found for the ultraviolet cascade with room air, in contrast to ultrafiltered air. Equal hydrocarbon concentrations were added to both air samples, whereupon the room air gave a higher yield of a-

colloid. With ultrafiltered air, the ultraviolet cascade was inactive at times, even giving zero yields. Often reproducibility of S reached only $\pm 1\%$ deviation, but often also deviations by factors of $1/2$ or 2 were observed.

The ultraviolet cascade became inactive in prolonged runs at low hydrocarbon concentrations and lower humidities up to 60% rh. Activity was maintained whenever natural aerocolloids, ammonia traces, or high hydrocarbon concentrations and high humidity were present, all of which favor high yields. Inserting a jacket of polyethylene or aluminum foil and solvent-cleaning of the lamps were of no consequence, showing the absence of wall effects.

Rapid deactivation was achieved with acetone vapor or a large unbranched flow of dry ultrafiltered air (20% rh) through the stages. The cascade was reactivated with 40 ppm of a reactive hydrocarbon.

The activity of the cascade seems, therefore, to depend on the presence of some condensation nuclei to start the reaction. An active cascade shows no particle background with the Royco photometer.

Humidity, next to hydrocarbon concentration, is the major factor governing the size of S or formation of aerocolloid. In turn, the degradability of deposits by aging or ultraviolet irradiation depends on the humidity level during formation of the aerocolloid. It was found that high humidity stabilized the deposits.

Aerocolloid formation increases with humidity despite lower

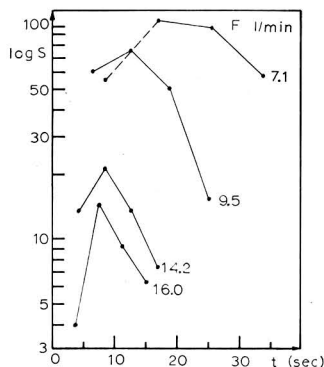


Figure 7. Aerocolloid yields vary with flow rates F and exposure t
Toluene 10 ppm, four lamps, 75% rh, slide speed τ 3, one-track deposition mode, F flow rates in ultraviolet cascade

Table I. Humidity Effect, Toluene

Four lamps, concentration 10 ppm at initial flow $F = 9.5$ l./min, slide speed τ 3

Stage	Total exposure, sec	S at 15% rh	S at 30% rh	S at 54% rh	S at 70% rh	S at 83% rh
A	6.3	1.78	5.05	10.5	44.5	182
B	14.6	11.1	20.2	28.4	82.0	215
C	26.8	8.40	12.8	18.0	50.5	129
D	49.9	1.60	5.00	7.80	26.8	43.0

oxidant concentrations. A plot of S vs. t at different humidities is similar to Figure 8 for the different flow rates F , where low F corresponds to high relative humidity. The effect of humidity at constant exposure is illustrated in Table I.

Water vapor should be considered as a reactant, since it can react with oxidant, hydrocarbon, and aerocolloid particles.

Reactivity of Hydrocarbons. Hydrocarbons of four or less carbon atoms and the respective oxo compounds (alcohols, acetone, methyl ethyl ketone) are unreactive.

Pure propane C_3H_8 and methane CH_4 were completely inert at 430 and 950 ppm. At 80% rh, in presence of such otherwise undetectable traces of toluene as would slowly evolve from the short Tygon connections of the HC dilutor, both hydrocarbons produced low yields of aerocolloids at concentrations of 45, 300, and 430 ppm. In these tests, methane gave a $t_{max} = 15$ sec, whereas propane with $t_{max} = 100$ sec joined the trend of the other unreactive hydrocarbons.

A comparison of unreactive substances was possible under the most favorable conditions (Table II). This gave a falling order of reactivity: *trans*-butene-2, ethylene, propylene, acetylene, propane, methane.

Studies on the relative reactivity of hydrocarbons with six or more atoms in the carbon chain were conducted at low concentration and a humidity of 60% rh. At higher humidity (80%), much higher S values were obtained, which lent themselves less to a wide comparison of compounds.

For the evaluation of reactivity, the deposit densities (τ 4-1) were considered at a level below the occurrence of co-

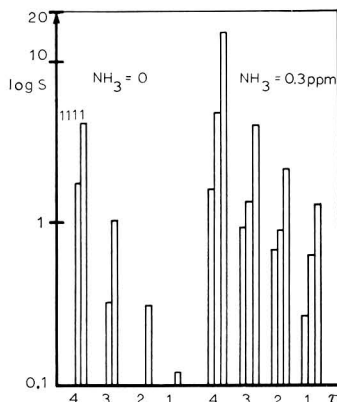


Figure 8. Deposit profile of aerocolloid from gasoline 200 ppm alone, and with added 0.3 ppm of NH_3

Four lamps, ultrafiltered air, initial flow F 9.6 l./min, 60% rh, exposures in A, B, C, D 7.4, 17, 29, 49 sec. Note absence of deposit from stages A, B without NH_3 , and from stage A with NH_3

Table II. Unreactive Hydrocarbons Compared

Four lamps, two-track deposition, hydrocarbon concentration 430 ppm, initial flow $F = 4.7$ l./min, slide speed τ 1, 80% rh

		S at 40 sec	S at 63 sec	S at 88 sec
<i>trans</i> -Butene-2	C_4H_8	0	3.70	...
Ethylene	C_2H_4	0	2.10	23.0
Propylene	C_3H_6	0	1.23	10.0
Acetylene	C_2H_2	0	1.13	5.83

alescence. The maximum-bearing stage (t_{max}) and the S -level at the maximum were noted.

The obtained sequence (Table III) agrees with that from S_R data for airborne aerocolloid. However, no useful relation between S and S_R was found, as the latter data depend on the concentration of hydrocarbon and stay small at the low concentrations used. Also, S represents only back-scattering, S_R forward- and back-scattering.

The tested higher hydrocarbons range in the order of falling reactivity in the ultraviolet cascade as follows: turpentine, cumene, cyclohexene, cyclohexane, xylene, toluene, benzene, octene, octane, benzaldehyde, gasoline.

All tests were run at $F_t = 9.6$ l./min with four ultraviolet lamps. The average suction demand per slit of the impactor was 2.3 l./min. Thus the exposures were 6.3, 14.5, 26.5, and 48.7 sec for the four consecutive deposits.

Cumene (isopropylbenzene) and turpentine were in a class by themselves and required only $1/5$ of the concentration used for all other substances. Cumene aerocolloid is notably resistant to degradation as compared with turpentine.

Cumene C_9H_{12} differed from other hydrocarbons (toluene, turpentine) in regard to the humidity effect. The results (Table IV) are similar to the dark reaction of turpentine by the almost constant S -level at $\leq 50\%$ rh. At high humidity, the low levels at B and D suggest partial coalescence.

Table III. Reactive Hydrocarbons Compared

Four lamps, initial flow $F = 9.6$ l./min, slide speed τ 4

HC	Ppm	Rh	S at				S_R at D
			A	B	C	D	
Turpentine	0.5	60	77	54	37	6.6	7
Cumene	0.5	56	78.5	62.0	84.0	17.5	...
Cyclohexene	2.5	60	170	110	73	31	0.3
Cyclohexane	2.5	60	48	92	48	17.5	1.0
Xylene	2.5	60	5.70	6.71	3.72	1.35	0.25
Toluene	2.5	60	0.61	1.22	1.52	0.64	0.05
Benzene	2.5	60	0.13	0.36	0.31	0.21	0.2

Table IV. Humidity Effect, Cumene

Four lamps, concentration 0.5 ppm, initial flow $F = 9.6$ l./min, slide speed τ 1

Test no.	Rh, %	S in stage			
		A	B	C	D
1487	18	0.00	4.03	5.40	3.27
1488	28	7.03	9.67	3.60	2.47
1489	36	6.53	9.07	4.73	2.90
1485	56	11.3	8.80	12.3	1.57
1486	75	123	86.7	107	2.00

Turpentine C₁₀H₁₆ consists of terpenes, unsaturated cyclic hydrocarbons with side chains, and is most reactive. Sizable yields of aerocolloids were obtained at 0.1–0.5 ppm turpentine vapor, as compared with 5 ppm for toluene.

Data for the less reactive hydrocarbons are summarized in Table V, which shows both the higher concentrations required and the effect of humidity.

It is necessary to compare compounds like octene and octane at several different humidities. The latter is less reactive, but rising humidity shows a greater effect with it.

Gasoline of regular grade with a vapor pressure of 490 mm Hg at room temperature was relatively unreactive. Sizable deposits were obtained at about 500 ppm, at long exposures only. This contrasts with car exhaust studies, where eighty-fold increases over the natural level were obtained. The difference may be due to the use of filtered air in the artificial mixture (absence of nucleating matter) and to reformation of hydrocarbons in the combustion process.

Effect of Ammonia. Discrepancies between sizable buildups of aerocolloids on ultraviolet irradiation of natural air and relatively large hydrocarbon concentrations required for a matching performance in laboratory testing precipitated a search for trace components other than hydrocarbons, which could increase or decrease the formation of aerocolloids.

Carbon dioxide had no influence, but sulfur dioxide showed a weak positive effect, and ammonia a strong one. The lowest level of hydrocarbon to produce aerocolloid in filtered air with the aid of humidity alone was 0.1 ppm of turpentine. This sensitivity increased much further with ammonia at levels of 0.3 to 5 ppm, and at high levels of ammonia the deposits were thick in the presence of the smallest traces of hydrocarbon. Such deposits showed a high degradability under ultraviolet irradiation, whereas deposits from traces of ammonia and higher hydrocarbon concentrations showed little degradability.

Ammonia at low concentrations enhanced the aerocolloid formation at $\geq 50\%$ rh, especially at high humidity. Systematic studies of hydrocarbon reactivity in presence of ammonia included benzene, cyclohexane, cyclohexene, gasoline, toluene, turpentine, xylene (Table VI), and room air (Table VIII).

Low traces of HC below normal reactivity level can yield impactable aerocolloids with ammonia (Table VII).

Benzene at 2.5 ppm is rather unreactive by itself, but it is active with ammonia at higher humidity. Cyclohexane is more reactive than benzene, and cyclohexene is reactive. Gasoline is quite inert, but it reacts in the presence of ammonia traces.

The great reactivity of turpentine stands out and here the shift of t_{\max} due to ammonia appears clearly. The degradation is greatly lessened by ammonia.

The effect of 0.3 ppm of ammonia with 200 ppm of gasoline

Table V. Less Reactive Hydrocarbons Compared

Four lamps, initial flow $F = 9.6$ l./min, slide speed $\tau = 4$

HC	Ppm	Rh, %	S at stage				S_R at D
			A	B	C	D	
1-, 2-Octene	10	60	17	42	14.2	1.75	2.5
	10	80	34	59	33	1.70	3
Octane	10	60	1.02	6.0	1.72	0.88	1.0
	10	80	24	104	48	6.5	0.8–1
Benzaldehyde	10	45	0.63	2.80	2.40	0.58	1–2
	10	80	26.5	51	45.5	86	1–2
Gasoline	200	60	0	0	1.80	4.30	3

Table VI. Ammonia Effect

Four lamps, 60% rh, initial flow $F = 9.6$ l./min, slide speed $\tau = 1$

Test no.	Ppm HC	NH ₃ solution	Scattering S of deposits from stage				S_R at D
			A	B	C	D	
Benzene							
1206	2.5	...	0	0.03	0	0	...
1207	2.5	1/50	0.54	3.20	5.60	2.43	...
Cyclohexane							
1216	2.5	...	0	1.90	2.60	2.30	
1151	2.5	1/100	1.39	5.87	3.43	0.95	1–2
1178	2.5	1/50	10.7	57.0	118	120	15–20
Cyclohexene							
1166	2.5	...	6.60	6.80	2.60	0.52	1–2
1167	2.5	1/100	47.3	55.0	35.0	14.0	1.5–2
Gasoline, regular							
976	200	...	0	0	0	0.12	3
977	200	1/100	0	0.27	0.65	1.33	
Toluene							
1180	2.5	...	1.93	2.57	1.27	0.10	0.3–4.0
1181	2.5	1/50	1.69	5.65	15.1	65.5	20–30
Xylene							
1190	2.5	...	0	0.22	0.02	0.05	
1179	2.5	1/50	1.80	7.30	1.3	21.7	...
Turpentine							
1009	0.5	...	2.90	3.90	1.43	0	4
1016	0.5	1/100	11.0	10.7	6.20	2.60	8–15
1011	0.5	1/50	6.70	20.0	43.0	24.0	10

Table VII. Ammonia Effect at Low Hydrocarbon Levels

Four lamps, hydrocarbon concentration 0.5 ppm, 60% rh, initial flow $F = 9.6$ l./min, slide speed $\tau = 3$

Test no.	Hydro-carbon	NH ₃ solution	S at			
			A	B	C	D
1221	Cyclohexene	...	0	0	0	0
1221	Cyclohexene	1/50	4.70	19.6	24.5	31.1
1220	Cyclohexane	...	0	0	0	0
1220	Cyclohexane	1/50	0.91	8.50	15.6	20.2

is shown in Figure 8 as an example for activating of unreactive hydrocarbons, in absence of nucleating matter. Ample leeway for both humidity and ammonia levels is noted here to point out that much larger effects can be achieved.

Studies on room air with and without added ammonia traces (0.3 ppm) indicated the presence of low hydrocarbon traces (Table VIII). The resulting aerocolloid formation was comparable to that obtained in clean ultrafiltered air with a measurable hydrocarbon concentration and added ammonia (0.3 ppm), but here the effect of nucleating matter came to aid.

Increased aerocolloid formation with room air in contrast to ultrafiltered air was found in a smaller measure directly, by adding equal hydrocarbon concentrations to such air samples, without ammonia.

Dark Reaction of Turpentine. Some formation of aerocolloid in a darkened stage was observed with toluene, at short exposures ($t < t_{\max}$) in the first stage of the ultraviolet cascade. To determine whether the reaction would occur without light energy, a turpentine-air stream was made to join an oxidant

Table VIII. Ammonia Effect with Room AirInitial flow: $F = 9$ l./min, slide speed τ 2, 37% rh

Test no.	Lamps in ABCD	NH ₃ solution	A	B	C	D
1019	0000	...	0.59	0.26	0.29	0.33
1020	0000	1/100	0.85	0.83	0.41	0.59
1021	0111	...	0.32	0.34	0.87	0.49
1022	0111	1/100	0.47	1.20	5.30	3.30

stream at the inlet of the dark stage C. Deposits from dark stages C and D showed a large formation and an absence of degradation. The oxidant stream, made from ultrafiltered air of the compressor line, contained $>10^7$ nuclei/cc, whereas before irradiation the instrument showed no reading for condensation nuclei. The dark reaction consisted thus in the growth of numerous nuclei to particle size.

Humidity appears to have no effect, except at $\geq 50\%$ rh. There, two effects are observed, a dark decay of oxidant leading to higher yields of aerocolloid (Table IX, nos. 1321, 1324) and a rise as usual (nos. 1439-42). Below 50% rh the yields are high and constant, apparently owing to the inability of the ozone to attack the aerocolloid in the dark.

The effect of a change in humidity on the dark reaction is shown in Table X. The second value of relative humidity is the result of mixing two equal flows of different humidities; thus 80 and 56 give 68 (80-68). It was found that large humidity shifts cancel the formation of impactable aerocolloid. The study was extended to lower humidities and smaller shifts, both up and down, alternating with constant humidity tests.

The effect of the humidity shift on an aerocolloid, present in impactable form, was studied by introducing the turpentine at stage A. An airstream of different humidity was introduced at stage C. The results are presented in Table XI, whereas the results from a fully lighted ultraviolet cascade, with impaction from the A, D stages, are presented in Table XII.

Results of Table XI have to be viewed with the consideration that the deposits C and D are remnants of an aerocolloid produced under ultraviolet light at 80% rh from 5 ppm tur-

Table IX. Dark Reaction at Constant Relative HumidityTurpentine 2.5 ppm of total air, added at stage C; τ 1; $F_{ox} = 3$ l./min, $F_{HC} = 3$ l./min; exposures AB-CD = 20, 20, 10, 17 sec. Hyphen separates oxidant stream and joint stream

Test no.	Lamps in AB-CD	Rh, %	S in C	S in D	D/C
1321	10-00	56-56	58.0	89.6	1.54
1324	01-00	56-56	41.2	68.4	1.66
1326	11-00	56-56	80.0	102	1.28
1417	10-00	28-28	41.1	66.3	1.61
1418	01-00	28-28	42.1	66.3	1.57
1419	11-00	28-28	86.0	103	1.20
1439	01-00	81-81	86.6	218	2.52
1440	01-00	71-71	76.3	197	2.58
1441	01-00	64-64	53.8	168	3.12
1442	01-00	56-56	67.0	151	2.25
1443	01-00	48-48	29.6	65.6	2.22
1444	01-00	40-40	31.8	66.4	2.08
1445	01-00	34-34	31.7	67.9	2.14
1446	01-00	28-28	33.7	65.8	1.95
1455	01-00	18-18	34.3	55.0	1.60

pentine. These equal the dark-reaction products obtained from 2.5 ppm turpentine at 50% rh. Thus, an enormous degradation has taken place in the 80-50% humidity stepdown.

Results of Table XII indicate that a full ultraviolet irradiation in the stages C and D did not overcome the effect of a humidity shift.

The described effect of humidity shifts has not been noted in the evaporative humidification of natural aerocolloids. However, natural humidity shifts definitely reduce the level of both the impactable aerosol and the condensation nuclei.

Results obtained with turpentine may not apply to other hydrocarbons, but the next less reactive substance, cyclohexene, which is about $1/10$ as reactive as turpentine, shows a similar humidity profile and effect of humidity shift (Table XIII).

Ammonia at a concentration of about 5 ppm was added to one of the airstreams in order to study any differences in

Table X. Effect of Humidity Shift on Dark ReactionTurpentine, 2.5 ppm of total air, added at stage C. $F_{ox} = F_{HC} = 3$ l./min each; τ 1. Hyphen separates oxidant stream and joint stream

Test no.	Lamps in AB-CD	Rh, %	S in C	S in D	D/C
1384	10-00	81-68	0	0	...
1390	10-00	80-50	0	0	...
1394	11-00	80-50	0	0	...
1282	10-00	20-50	0	0	...
1305	11-00	20-50	0.90	1.60	1.78
1413	10-00	18-23	0.35	0.23	0.66
1414	10-00	56-56	40.5	73.0	1.80
1415	10-00	28-28	41.4	69.7	1.68
1416	10-00	28-23	0	0	...
1426	10-00	13-10.5	0.18	0.53	2.94
1427	10-00	8-10.5	0.20	0.35	1.75
1428	10-00	8-8	59.0	83.0	1.41

Table XI. Effect of Humidity Shift on Ultraviolet ReactionLamp in A; turpentine, 2.5 ppm of total air, added at A, slide speed τ 1. Flows enter at A and C, 3 l./min each. Hyphen separates oxidant stream and joint airstream; rh given for joint stream is value of mixture

Test no.	Rh, %	S in C	S in D	D/C
1358	80-50	29.0	26.0	0.90
1523	80-80	189	201	100
1524	80-68	1.83	3.02	3
1525	50-50	58.2	54.7	400
1526	80-68	10.2	11.4	80

Table XII. Effect of Humidity Shift under Ultraviolet LightFour lamps. Turpentine 2.5 ppm of total air (6 l./min), impaction from A and D; flows F in A, B, C, D = 3.0, 0.5, 3.5, 3.5 l./min, slide speed τ 1, hyphen marks junction of flows

Test no.	HC inlet	Rh, % in AB-CD	S in A	S in D	S_R in D
1515	A	80-80	47.3 ^a	183	
1516	C	80-80	...	187	
1517	A	80-50	200	0.45	
1518	C	20-50	...	0	4
1519	C	80-68	...	0	1

^a Diminished by coalescence.

relation to the effects observed in the ultraviolet cascade (Tables XIV and XV). For constant humidity it appears from Table XIV that ammonia added at *A* raises the yield (*S*) about sixteenfold. However, added at *C* in the dark, ammonia reduces the yield to about $1/3-1/6$. The positive effect is of a different size for 10 and 01 settings, being smaller for the latter, at the humidity applied.

At the conditions of a humidity shift, the addition of ammonia to the ultraviolet reaction did not change the picture, which means that a large positive ammonia effect took place in *AB* and was then wiped out (compare Table XV with Table XI, no. 1358).

Qualitative tests at 34–57% rh showed no significant effect of ammonia, except for a slight modification of deposit traces which was of a sign opposite to the major changes reported in Table XIV.

The dark reaction was faster with two ultraviolet lamps ($D/C < 1.5$) than with one ($D/C \geq 1.5$), apparently owing to the higher oxidant concentration. It was shown, for 50% rh,

Table XIII. Dark Reaction of Cyclohexene

Lamp in *A*: cyclohexene added at *C*, slide speed τ 1, flows *F* in *A*, *B*, *C*, *D* = 3.0, 3.0, 6.0, 3.5 l./min. Hyphen marks junction of flows

Test no.	Rh, % in <i>AB-CD</i>	<i>S</i> from <i>C</i>	<i>S</i> from <i>D</i>	<i>D/C</i>	Cyclo- hexene, ppm of total air
1468	56-56	0	0	...	2.5
1470	56-56	0.20	0.30	1.50	5.0
1472	34-34	0	0.13	...	10
1473	18-18	0	0.57	...	10
1474	56-56	0.39	1.38	3.54	10
1475	81-81	7.50	21.5	2.86	10
1476	81-57	0	0	...	10

Table XIV. Dark Reaction and Effect of Ammonia at Constant Relative Humidity

NH₃ (~5 ppm) added at *A* or *C* (italicized flows), turpentine 2.5 ppm of total air added at *C*; with airflows of 3 l./min each entering at *A* and *C*. Hyphen in second column indicates junction of flows, 1./min each; rh in *AB-CD*, 56–56%

Test no.	Lamps in <i>AB-CD</i>	<i>S</i> from <i>C</i>	<i>S</i> from <i>D</i>	<i>D/C</i>
1342	10-00	15.8	31.0	1.96
1343	10-00	258	265	1.03
1348	10-00	8.55	19.7	2.30
1362	01-00	29.0	63.1	2.18
1363	01-00	201	254	1.26
1352	01-00	6.03	12.0	1.99
1458	11-00	56.4	78.7	1.40
1431	11-00	205	222	1.08
1459	11-00	46.7	77.2	1.65

Table XV. Ultraviolet Reaction and Ammonia Effect in a Humidity Shift

NH₃ (~5 ppm) added at *A* or *C* (italicized flows) turpentine (2.5 ppm of total air) added at *C*; hyphen indicates junction of two flows, 3 l./min each. Rh in *AB-CD*, 80–50%

Test no.	Lamps in <i>AB-CD</i>	<i>S</i> from <i>C</i>	<i>S</i> from <i>D</i>	<i>D/C</i>
1367	10-00	11.8	11.1	0.94
1368	10-00	21.3	21.3	1.00
1371	10-00	20.5	19.7	0.96

that a Vycor lamp in stage *C* accelerated the reaction to the same yield as two stages *C* and *D* of darkness. Since further irradiation in *D* was not effective, the reaction was completed.

The reactivity of turpentine in the dark reaction is about tenfold that of cyclohexene, since 2.5 ppm of turpentine gave strong deposits and 10 ppm of cyclohexene gave weak deposits. The corresponding ratio in the ultraviolet reaction is five, where the maximum of *S* at t_{max} is the object of comparison. It appears that the reactivity gap is widened in the dark.

In the ultraviolet cascade, small concentrations of ammonia changed the profile of yields by reducing the degradation of aerocolloids. Thus, the *S* maxima were shifted from the first to the fourth stage, for the three most reactive substances. High humidity has a similar effect. However, ammonia reacts easily with oxidant and ultraviolet, and both effects may, therefore, hinge on nucleation and modification of some of the oxidant, rather than action on aerocolloid particles.

In the dark reaction, the ammonia effect was the same as in the ultraviolet cascade when ammonia was involved in the ultraviolet-oxidant process. Obviously, all ammonia (5 ppm) was gone before the reaction of oxidant and hydrocarbon, but that reaction was greatly enhanced.

Ammonia in the HC stream of the dark reaction was not reacting with oxidant; it reduced instead the aerocolloid formation. This is viewed as an effect analogous to that of the humidity shift.

The humidity shift of few percent either way eliminated the formation of precipitable aerocolloid, both in the dark and under ultraviolet light. Aerocolloid already formed was reduced or eliminated (Tables X and XI).

These results, fortified by day profiles of natural aerocolloid levels, illuminate the role of humidity in the formation of aerocolloids under any conditions. The constancy of humidity over sufficient time intervals should be a basic requirement for the formation of aerocolloids in nature or experiment. Inversely, the inconstancy of humidity, as in the "burning off" of fog and haze by warming sunshine, provides a major mechanism for the degradation of aerocolloids.

Aerocolloid deposits obtained in the moving-slide impactor show little change for many hours. Storage in a refrigerator in closed plastic containers prolongs their usefulness. Even so, changes occurred in some slide deposits by coalescence or desiccation, with loss of light-scattering power.

All degradation procedures resulted in a lowering of the light-scattering *S*, except in a final drying with formation of a solid residue. Degradation by desiccation was significant only in aerocolloids obtained at a high humidity. Degradation by prolonged ultraviolet irradiation was strong with deposits obtained at low humidity rather than at high humidity. This degradation was caused by oxidant and light, as shaded areas were barely attacked (glass jar). Deposits were also degraded along sharp outlines under slits and shades mounted with an ultraviolet lamp (Penray) over a microscope stage.

Deposits of natural aerocolloids tend to leave a mineral residue, which retains a fraction of the original light-scattering power. The artificial aerocolloids produced from hydrocarbon vapor and ultrafiltered air are completely volatilized by prolonged ultraviolet irradiation. The degradability of a deposit depends on treatment intensity and duration, the conditions of formation, deposit density, and the nature of the aerocolloid.

The degradability varies by several orders of magnitude for both natural and artificial aerocolloids. It is a sensitive and distinctive property of a deposit.

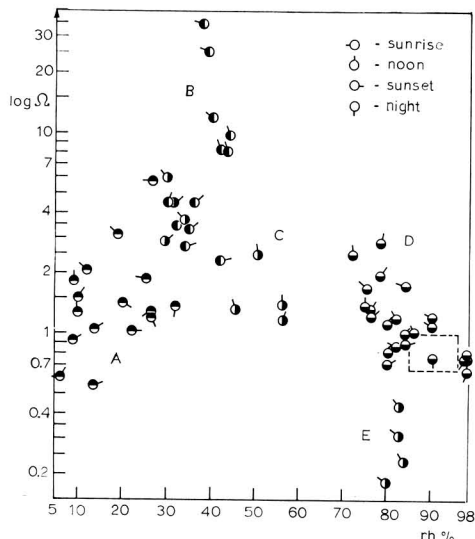


Figure 9. Ω -Variations with relative humidity at various test sites, times, and temperatures

Insert contains 25 tests. Ω is the ratio of S from irradiated and non-irradiated humidified air samples

Sites symbols: circles solid at top - A; on left - B; on right - C and E; at bottom - D. Site A: Northern border of Los Angeles basin, street level in Altadena, 1100 ft elevation; 6-32% rh; T , 60-92°F. Site B: Northern ridge of Los Angeles basin, near Mt. Wilson, 5500 ft; 30-42% rh; T , 76-84°F. Site C: Slope between A and B sites, 2100 ft; 25-56% rh; T , 70-89°F. Site D: Coastal Promontory, Point Vicente, 200 ft; 72-98% rh; T , 60-73°F. Site E: Site C with overcast skies; 80-84% rh; T , 48-49°F.

For reactive hydrocarbons, the degradability was highest in the product of stage A and decreased for the later stages. For cyclohexene (5 or 20 ppm) the residual S after 1 hr ultraviolet irradiation was 3, 5, and 11%, for rh at formation 20, 45, 80%, respectively. Cyclohexane gave a distinctly smaller degradation and the less reactive deposits from toluene persisted through a 16-hr treatment. Many marine deposits were as degradable as those of cyclohexene.

During land and sea expeditions tracing hydrocarbon and weather patterns, the ultraviolet cascade method permitted the distinguishing of slight differences of the air masses by com-

paring characteristic buildup profiles and degradability of deposits from several stages of the cascade.

In Figure 9, the effect of ultraviolet irradiation is shown in terms of Ω , the ratio of S level under long ultraviolet exposure (four lamps) to that under one-lamp exposure (practically the original, nonirradiated level). All air samples were humidified. The ratio Ω is plotted against the prevailing ambient relative humidity.

The high Ω values B in a forest sunrise indicate the presence of relatively high levels of unreacted gaseous hydrocarbons, in contrast to the afternoon situation. Forty percent relative humidity seems to be most favorable for aerocolloid formation. A lowering of Ω during the later daytime and night is indicated. Tests E reflect an arrival of sea air and rising humidity. Ratio $\Omega > 1$ is rarely observed above 80% rh (mornings only).

These examples may illustrate the range and variety of characters of air masses which are accessible by the present new method. The strong effects of polluted air have been illustrated by Goetz (1969). The use of Vycor shields may provide a further distinction. The effect of Vycor irradiation was not significant in car exhaust, which holds much HC and humidity. However, outdoor air can show a slight Vycor irradiation effect. In these cases, only Vycor lamps were used and the oxidant was provided by the natural sunlight reaction.

Acknowledgment

The authors wish to acknowledge the collaboration of George Mylonas and David Williams, Jr., and the assistance of Mrs. Sybille Waiyaki. The ultraviolet cascade (Goetz) and flow alternator were developed at ARG with the assistance of Harry Garand.

Literature Cited

- Goetz, A., ENVIRON. SCI. TECHNOL., **3** (2), 154-60 (1969).
- Goetz, A., Klejnot, O. J., *J. Air Pollut. Contr. Ass.*, **17**, 602-3 (1967).
- Goetz, A., Pueschel, R. F., *J. Air Pollut. Contr. Ass.*, **15** (3), 90-5 (1965).
- Goetz, A., Pueschel, R. F., *Atmos. Environ.*, **1**, 287-306 (1967).
- Haagen-Smit, A. J., *Ind. Eng. Chem.*, **44**, 1342 (1952).
- Haagen-Smit, A. J., Bradley, C. E., Fox, M. M., *ibid.*, **45**, 2086-9 (1953).
- Haagen-Smit, A. J., Bradley, C. E., Fox, M. M., *ibid.*, **48**, 1884-7 (1956).

Received for review July 17, 1970. Accepted July 28, 1971. This project was supported by the National Air Pollution Control Administration under Grant no. 2 R01 AP 00543-03.

Reinvestigation of the Jacobs-Hochheiser Procedure for Determining Nitrogen Dioxide in Ambient Air

Larry J. Purdue, Jared E. Dudley,¹ John B. Clements,² and Richard J. Thompson

Division of Air Quality and Emission Data, National Air Pollution Control Administration, Environmental Health Service, U.S. Public Health Service, U.S. Department of Health, Education and Welfare, Cincinnati, Ohio 45226

■ Problems with the determination of ambient air concentrations of NO₂ by absorption in NaOH solution (Jacobs-Hochheiser procedure) lead to a reinvestigation of the method. Permeation tubes were used to generate atmospheres containing known amounts of NO₂ at ambient air levels which were sampled by the Jacobs-Hochheiser procedure. It is shown that nitrate ions are not generated on sampling these atmospheres and no account need be made for their presence in using the Jacobs-Hochheiser procedure. The Na₂CO₃ generated on sampling must be carefully considered in an analytical procedure involving a hydrazine reduction to determine nitrate ions. Overall analytical efficiency for the Jacobs-Hochheiser procedure, as carried out in this investigation, is 35%. Surface active agents cannot be used, because of excessive foaming. It is shown that fritted glass bubblers give higher precision than glass-restricted orifices.

Nitrogen dioxide, a widespread air pollutant of major importance, can be determined in ambient air using dilute sodium hydroxide as a collection medium. The procedure, commonly referred to as the Jacobs-Hochheiser procedure, has been automated (Jacobs and Hochheiser, 1958) but has found its widest application as an integrated sampling method for use in a network operation, such as the National Air Surveillance Network, where relatively long sampling periods (up to 24 hr) and return of the samples to a central laboratory are required. These requirements prohibit the use of the more common procedure (Saltzman, 1954) in which a fairly unstable azo dye is formed directly with nitrogen dioxide during sampling. Poor collection efficiency, variable stoichiometry (Morgan et al., 1967), and poor correlation with the continuous monitoring method based on the Saltzman procedure, strongly suggested that the integrated Jacobs-Hochheiser method for ambient air nitrogen dioxide determination deserved reinvestigation.

Integrated Jacobs-Hochheiser Method

In the integrated Jacobs-Hochheiser method, air containing nitrogen dioxide is drawn through a dilute (approximately 0.1N) sodium hydroxide solution for a sampling period of up to 24 hr. This operation supposedly produces a dilute solution of sodium nitrite and sodium nitrate in the absorbing solution. The ambient air concentration of nitrogen dioxide is determined by analyzing for nitrite ion using the classical diazotization and coupling procedure to form a deeply colored azo dye. The transmittance of the resulting azo dye solution is

measured and compared to the transmittance of solutions of properly developed sodium nitrite standards made up in the same concentration of sodium hydroxide.

The degree of conversion of nitrogen dioxide gas to nitrite ion must be known in order to calculate the concentration of nitrogen dioxide in the air samples. Morgan et al. (1967) determined the degree of conversion by sampling ambient air at 13 urban sites, analyzing for sodium nitrite and sodium nitrite plus sodium nitrate, then calculating the ratio of the nitrite alone to the total nitrite plus nitrate. They found the ratio to be 0.63. To account for unabsorbed nitrogen dioxide, Morgan et al. (1967) independently determined the collection efficiency by passing ambient air through a series of five absorbing solutions and comparing the nitrite plus nitrate in the first absorber with the total nitrite plus nitrate in the other four. They found the collection efficiency to be 50%. The National Air Surveillance Network used the results of the Morgan et al. (1967) study to develop an analytical method for determining nitrogen dioxide concentrations in ambient air.

The data previously collected by the National Air Surveillance Network showed that the degree of conversion is subject to wide variation and can, therefore, be a significant source of error. If, however, the collected nitrate were reduced to nitrite before analysis so that nitrite and nitrate would both be determined, this source of variation should be significantly reduced and a decrease in experimental error should result. The work reported here described experiments designed to obtain an improved nitrogen dioxide determination using a nitrate reduction procedure.

Procedure

Standard Nitrogen Dioxide Atmospheres. Permeation tubes (O'Keefe and Ortman, 1968; Scaringelli et al., 1970) were used to generate sub-ppm atmospheres of nitrogen dioxide. These levels of nitrogen dioxide were prepared by passing a slow stream (ca. 200 ml/min) of dry, NO₂-free air over a calibrated permeation tube held at an appropriate temperature and diluting the resulting airstream with dry, NO₂-free air to the four concentrations shown in Table I. In contrast to the

Table I. Conditions for Generating Known Atmospheres of Nitrogen Dioxide

Permeation tube temp, °C	Nitrogen dioxide permeation rate, µg/min	Air dilution rate, l./min	Nitrogen dioxide concentration, µg/m ³ (ppm) ^a
5.45	0.726	8.854	82 (0.044)
5.45	0.726	4.774	152 (0.081)
15.95	1.797	8.854	203 (0.108)
15.95	1.797	4.774	376 (0.200)

^a µg/m³ = (µg/min)/(l./min) × 10³; ppm = (µg/m³) × 5.32 × 10⁻⁴ at 25°C and 760 mm Hg.

¹ Present address: University of Idaho, Moscow, Idaho 83843.

² Present address: Environmental Protection Agency, Research Triangle Park, N.C. 27711. To whom correspondence should be addressed.

experience of other workers (Scaringelli et al., 1970), no difficulty was encountered in using nitrogen dioxide permeation tubes at temperatures down to 5.45°C.

Air Sampling. The National Air Surveillance Network's 24-hr integrated gas sampler (Morgan et al., 1967) was used to collect samples from the standard atmospheres. Uprturned, 70- to 100- μ sintered glass frits and glass-restricted orifices (0.35 ± 0.05 mm i.d.) were each evaluated as dispersers for the airstream entering the collection reagent (0.25N NaOH). A surfactant dispersing agent (Carbowax 6000) was also evaluated as an aid to increase nitrogen dioxide absorption but it gave inconsistent results at the levels of Carbowax that could be used without causing excessive foaming. Ten samples, each collected over a 24-hr period at a sampling rate of 200 ml/min, were taken for each run.

Analysis. All analyses were done by an automated procedure. To determine nitrite plus nitrate, a copper-catalyzed, basic hydrazine reduction procedure based on the method of Kamphake et al. (1967) was developed to give equal responses for equimolar amounts of both nitrite and nitrate. The same sodium hydroxide solution used to absorb the nitrogen dioxide was used as the source of base for the hydrazine reduction. The flow patterns and reagent concentrations are shown in Figure 1. To determine nitrite alone, the analysis was carried out without nitrate reduction by substituting distilled water for hydrazine. Sodium nitrite and sodium nitrate standards were made up to contain 0.25, 0.50, 1.0, 1.5, and 2.0 $\mu\text{g NO}_2^-/\text{ml}$.

Results and Discussion

Reevaluation of the Integrated Jacobs-Hochheiser Method. Initial work in the reevaluation was directed to reducing the nitrate to nitrite before analysis, thus eliminating variability in the ratio of these two ions as a source of error. Four atmospheres containing sub-ppm levels of nitrogen dioxide (Table I) were sampled, and the amount of nitrite and nitrite plus nitrate present in each collected sample was determined.

Initially, our results agreed with Morgan et al. (1967), but then we realized an important error had been committed in both procedures because the effect of carbon dioxide in air had been ignored. Independent investigation showed that in a basic hydrazine reduction procedure, the analytical response for either nitrite or nitrate is higher in sodium carbonate than in sodium hydroxide, apparently due to differences in the rates of destruction of the nitrite by hydrazine. Since the carbon dioxide of air leads to the formation of sodium carbonate in the absorbing solutions, it is obvious that careful consideration must be given to the composition of the absorbing solution after sampling in order to obtain an accurate analysis. Previous procedure always had prepared nitrite standards in sodium hydroxide, but the above findings show that it is important that the standards be prepared in mixtures of sodium hydroxide and sodium carbonate which duplicate the composition of the collected sample. Sodium bicarbonate was shown to be absent and did not have to be considered.

Analyses were rerun with and without hydrazine, using properly prepared standards, and nitrite and nitrite plus

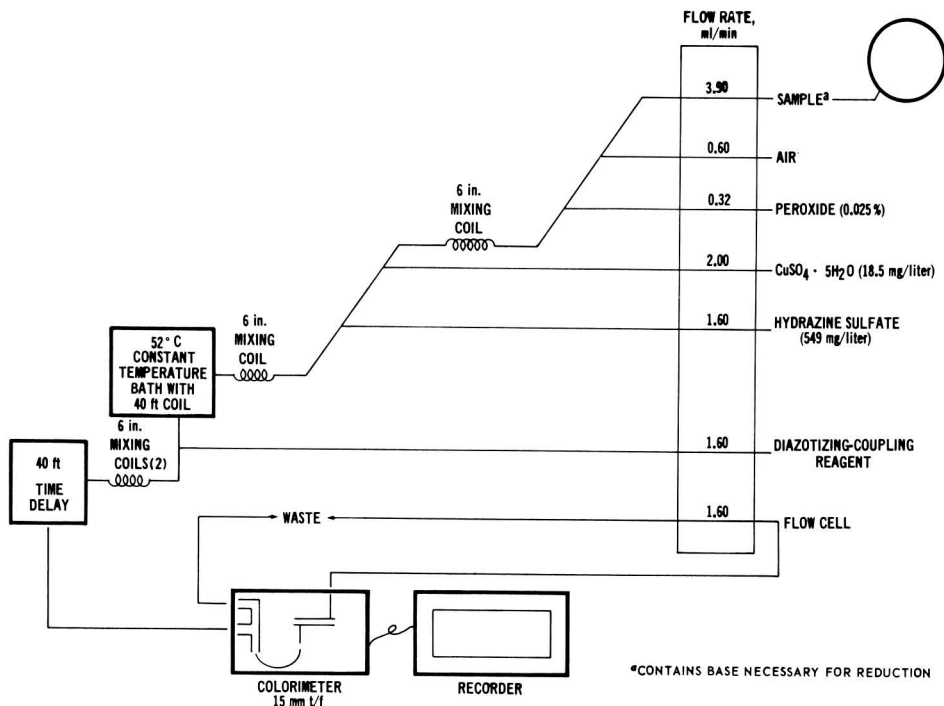


Figure 1. Automated analysis flow pattern for nitrogen dioxide

Sample time, 1 min
Washout time, 2 min

Diazotizing-coupling reagent: 20 g/l. sulfanilamide and 2.0 g/l. *N*-(1-naphthyl)ethylene diamine dihydrochloride in 10% (V/V) phosphoric acid in distilled water

Table II. Stoichiometric Factor as a Function of Nitrogen Dioxide Concentration^a

Nitrogen dioxide concentration, $\mu\text{g}/\text{m}^3$ (ppm)	Stoichiometric factor ^b
82 (0.044)	0.98
152 (0.081)	0.97
203 (0.108)	1.03
376 (0.200)	1.02

^a Standards prepared in solutions containing 9.5 g/l. sodium carbonate and 2.5 g/l. sodium hydroxide.

^b $\frac{\mu\text{g NO}_2^-/\text{ml}}{\mu\text{g NO}_2^-/\text{ml} + \mu\text{g NO}_3^-/\text{ml}}$

Table III. Recovery of Nitrogen Dioxide from Standard Atmospheres

	NO ₂ levels, $\mu\text{g}/\text{m}^3$ (ppm) ^a							
	82 (0.044)		152 (0.081)		203 (0.108)		376 (0.200)	
	Orifice	Frits	Orifice	Frits	Orifice	Frits	Orifice	Frits
Average, $(\bar{X})^b$	22.3	29.7	26.0	53.8	20.4	78.0	11.5	
Rel std deviation, $(S_{rel})^c$	15.4	19.9	25.2	10.8	25.4	11.9	15.6	
Recovery, $(R)^d$	27.2	36.2	17.1	35.4	10.1	38.5	30.6	

^a Calculated from: $\mu\text{g NO}_2/\text{m}^3 = (C \times A)/V$, where C = concentration of nitrite ion, $\mu\text{g}/\text{ml}$; A = volume of collection reagent, ml; and V = volume of air sampled, m³.

^b Replicate of 10.

^c $S_{rel} = (S/\bar{X}) \times 100$, S = std dev.

^d $R = (\bar{X}/\text{NO}_2 \text{ level}) \times 100$.

nitrate redetermined. The ratio $\text{NO}_2^-/(\text{NO}_2^- + \text{NO}_3^-)$, which is defined as the stoichiometric factor, was recalculated for each sample (Table II). Since there was no difference in response between analysis for nitrite and for nitrite plus nitrate, a stoichiometric factor of one was obtained. This leads to the conclusions that no nitrate is formed during sample collection and that overall variation can be accounted for by collection efficiency and analytical variation. Crecelius and Forwerg (1970) reported similar results in which they find that NO₂ in the sub-ppm range does not generate nitrate ion. A nitrate reduction procedure is, therefore, not only unnecessary but also impractical for use in network sampling because the amounts of sodium hydroxide, sodium bicarbonate, and sodium carbonate would also have to be determined for each sample in order to make accurate evaluations.

Additional Procedural Evaluations. In addition to eliminating the error due to variability in the stoichiometric factor, two other factors were investigated with hopes of improving the analysis. The first of these, the incorporation of Carbowax 6000, in the collecting solution to aid nitrogen dioxide absorption, gave inconsistent results at the levels of Carbowax that could be used without excessive foaming. The second factor investigated was the precision and efficiency of the device for dispersing the airstream in the collecting reagent. Glass-restricted orifices and sintered glass frits were compared.

In spite of quality control problems, difficulty in network use, and expense, past practice in air sampling for nitrogen dioxide indicates that fritted-glass devices are preferred for dispersing the airstream in the collecting reagents (Morgan et al., 1967; Saltzman, 1954). Meadows and Stalker (1966) reported that glass-restricted orifices provide higher analytical precision, albeit lower collection efficiency, than do fritted-tip devices. It was reasoned that some collection efficiency could be sacrificed for a gain in precision and that restricted-orifice dispersers deserved further investigation. The experimental results, shown in Table III, clearly show that frits are more efficient for nitrogen dioxide collection than are glass-restricted orifices. In addition, precision as shown by relative standard deviation, is also better with frits than with orifices, a finding contradictory to the one reported by Meadows and Stalker. This difference in precision may be a consequence of the use of different types of fritted-tip bubblers. Meadows and Stalker used 30- to 50- μ polyethylene-fritted bubbler, which gave poor precision (32.7% rel std dev). The 70- to 100- μ glass-fritted bubblers used for this study gave relatively good precision (14.5% rel std dev).

From the data of Table III, an overall analytical efficiency of 35% for the integrated Jacobs-Hochheiser method, as used in the National Air Surveillance Network, was calculated by averaging the four recovery values determined when frits were used to disperse the airstream. The report of a 15% conversion of nitrogen dioxide to nitric oxide on absorption into sodium hydroxide contributes an additional reason for the low efficiency of measured nitrogen dioxide absorption (Buck and Stratmann, 1967). Low efficiency remains the chief weakness of the integrated Jacobs-Hochheiser method for ambient air sampling and analysis of nitrogen dioxide, but, at present, there is no other practical method available for measurement of this pollutant in a network operation where analysis must be delayed.

Acknowledgment

We express our sincere appreciation to Richard E. Enrione for helpful advice on this problem and to Philip Greenland and Barbara Bonfield for valuable technical assistance.

Literature Cited

- Buck, M., Stratmann, H., *Staub.*, **27**, 11-15 (1967).
 Crecelius, H. J., Forwerg, W., *ibid.*, **30**, 23-5 (1970).
 Jacobs, M. B., Hochheiser, S., *Anal. Chem.*, **30**, 426-8 (1958).
 Kamphake, L. J., Hannah, S. A., Cohen, J. M., *Water Res.*, **1**, 205-16 (1967).
 Meadows, F. L., Stalker, W. W., *Amer. Ind. Hyg. Ass. J.*, **27**, 556-9 (1966).
 Morgan, G. B., Golden, C., Tabor, E. C., *J. Air Pollut. Contr. Ass.*, **17**, 300-4 (1967).
 O'Keefe, A. E., Ortman, G. C., *Anal. Chem.*, **38**, 760-3 (1968).
 Saltzman, B. E., *Anal. Chem.*, **26**, 1949-55 (1954).
 Scaringelli, F. P., O'Keefe, A. E., Rosenberg, E., Bell, J. B., *Anal. Chem.*, **42**, 871-6 (1970).
 Scaringelli, F. P., Rosenberg, E., Rehme, K. A., *ENVIRON. SCI. TECHNOL.*, **4**, 924-9 (1970).

Received for review October 27, 1970. Accepted July 16, 1971.

Environmental Air Analysis for Ultratrace Concentrations of Beryllium by Gas Chromatography

William D. Ross

Monsanto Research Corp., Dayton Laboratory, Dayton, Ohio 45407

Robert E. Sievers¹

Aerospace Research Laboratories, ARL/LJ, Wright-Patterson Air Force Base, Ohio 45433

■ A routine method of analysis for ultratrace concentrations of beryllium in particulate matter collected on air filters and in water is described. The particulate matter on the filters is ashed, the residue is digested with acid, and the resulting solution is buffered to the optimum pH for solvent extraction. Potential interfering metals are eliminated by masking with EDTA. A benzene solution of trifluoroacetylacetone [H(tfa)] is allowed to react with the beryllium in the aqueous solution to form Be(tfa)₂. The organic extract is injected into a gas chromatograph equipped with an electron-capture detector. The chromatographic peak resulting from Be(tfa)₂ formed from the unknown solution is compared with standard Be(tfa)₂ solutions for quantitation. The results indicate that the gas chromatographic method is more sensitive and reproducible than any other method now being used for the determination of beryllium in environmental samples. Analysis of air filters showed beryllium concentrations from 0.00016 to 0.00049 μg of Be/m³ of air in the 14 urban samples examined.

Analytical methods that can readily detect ultratrace levels of beryllium in air are urgently needed because of its high toxicity. Better environmental surveillance techniques are essential because of the widening use of beryllium in industry and space activities—e.g., rocket fuels. The chelation-gas chromatographic method for determining this metal in various media—e.g., water, biological fluids, and lunar soil—is well suited for ultrasensitive monitoring for beryllium in the environment. Instrumentation is relatively inexpensive, and the technique is easy enough to be readily conducted by trained technicians. A general review of metal analysis by gas chromatography can be found in a book by Moshier and Sievers (1965).

The gas chromatographic (gc) analytical method for determination of beryllium was first described in 1966 when lower limits of detection were found to be about 4×10^{-13} g [recently improved to about 4×10^{-14} g (Sievers et al., 1971)] where quantitative formation and extraction of Be from water by solvent extraction of the metal via chelation with trifluoroacetylacetone [H(tfa)] have been achieved (Ross and Sievers, 1968). Noweir and Cholak (1969) determined beryllium in biological tissues and in air by a similar method, and Taylor et al. (1968) have demonstrated that Be in small amounts of biological materials can be reacted directly with H(tfa) in glass capsules and determined quantitatively by gas chroma-

tography. The gc-chelation method has recently been used in the analysis of lunar soils, meteorites, and terrestrial samples for the quantitative determination of beryllium at sub-ppm levels (Sievers et al., 1971). The objective of the present investigation was to develop a rapid, ultrasensitive, and reliable analytical method for the analysis of beryllium in airborne suspended particulate matter collected on glass filters.

The gc method described in this paper has enough sensitivity to detect beryllium in all filter digests analyzed with sensitivity to spare. By the emission spectrographic method now used at Air Pollution Control Office, beryllium was detected in less than 15% of the samples examined.

Experimental

Reagents. 0.164M H(tfa) IN NANOGRADE BENZENE (MALLINCKRODT). This solution was made by diluting 2 ml of freshly distilled H(tfa) (Pierce Chemical Co.) in 100 ml of benzene. The solution was stored in a silanized, 100-ml borosilicate glass volumetric flask. Benzene solutions of H(tfa) and also neat H(tfa) are subject to slow decomposition on standing which produces spurious gc peaks.

3N NaOH SOLUTION FOR NEUTRALIZING REAGENT AND 0.1N NaOH BACKWASHING REAGENT. These solutions were prepared from Matheson, Coleman and Bell (MCB) analyzed RG NaOH and deionized water.

ETHYLENEDIAMINETETRAACETIC ACID (EDTA)-BUFFER SOLUTION. This solution was prepared by weighing out 5.15 g of Na₂EDTA · H₂O (G. F. Smith Chemical Co.), 85 g of NaOAc · 3H₂O (MCB, reagent), and 6.25 ml of glacial acetic acid (Baker, Ultrex) and dissolving these reagents in 500 ml of deionized water.

Standard Beryllium Solutions. Standard Be(tfa)₂ solutions were prepared by dissolving Be(tfa)₂, purified by sublimation, in Nanograde (Mallinckrodt) benzene. Further dilutions were made until the resulting concentration was 1.0×10^{-11} g of Be/μl. This solution was prepared every two weeks.

The standard aqueous beryllium solutions were prepared by dissolving a beryllium metal chip in concentrated HCl (Du Pont, reagent) and diluting with deionized water to an ultimate concentration of 9.2×10^{-12} g of Be(II)/μl.

Silanization of Glassware. The standard samples, Be(tfa)₂ and aqueous Be(II), were stored in borosilicate glass volumetric flasks which had been cleaned in Chromerge cleaning solution and then silanized to reduce any reactive sites. This was achieved by filling the flasks with a 20% solution of hexamethyldisilazane (HMDS) in benzene and letting them stand overnight. The reaction vessels (5-ml culture tubes) were treated by a similar method.

Preparation of Filter Digests. The air filter sample digests

¹ To whom correspondence should be addressed.

used in this investigation were obtained from the Division of Air Quality and Emission Data of the National Air Pollution Office (APCO). Samples were obtained by drawing known volumes of air through porous filters from various cities in the United States. Glass-fiber filters which retain particles as small as 0.3μ were used in conjunction with high volume samplers. Filter size was 7×9 in. of exposed surface. The filter permitted passage of between 50 and 60 ft³ of air/min. The filters analyzed had a total of 2200 m³ of air passed through them over a 24-hr period. One-inch strips were cut from these filters and were digested by the following procedure described by Thompson et al. (1970). The digestion portion of the method has been used by APCO routinely as the standard pretreatment procedure for metal analysis by emission spectrography.

The strips were placed in borosilicate glass boats and placed in a Tracerlabs low-temperature asher at about 150°C for 1 hr at 1 mm chamber pressure with an oxygen flow of 50 cc/min.

The ashed filter was placed in a glass thimble, and the thimble was placed in an extraction tube. A 125-ml Erlenmeyer flask was charged with 8 ml of constant boiling HCl (19%, Du Pont reagent grade) and 32 ml of HNO₃ (40%, Baker and Adams, redistilled ACS grade). The flask was attached to the extraction tube and the extraction tube was fitted with an Ahlin condenser. The acid was refluxed over the sample for 3 hr.

The extraction tube and the condenser were removed, and the flask was fitted with a thermometer adapter. The extracted liquid was concentrated to 1–2 ml on a hot plate, cooled, and allowed to stand overnight. This material was quantitatively transferred to a graduated 15-ml centrifuge tube with three washings of 5 to 10 drops of diluted acid. The samples were diluted to 4.4 ml with distilled water. The tubes were then centrifuged at 2000 rpm for 30 min, and the supernatant was transferred to polypropylene tubes ready for analysis.

Procedure for Gas Chromatographic Analysis. One milliliter of the aqua regia filter digest was accurately pipetted into a 5-ml borosilicate glass culture tube fitted with a screw cap. One milliliter of EDTA–sodium acetate buffer solution was added to the culture tube. Adequate amounts of a 3*N* NaOH solution were added to bring the pH to between 5.5 and 6.0. The requirement was between 0.8 and 1.3 ml, depending on the original pH of the digest.

The tube containing a small Teflon-coated magnetic stirrer was capped and inserted into an oil bath maintained at 93°C on a Corning stirring hot plate. The sample was heated and stirred vigorously for 10 min.

The tube was cooled, and 1 ml of 0.164*M* H(tfa) in benzene was added. The tube was capped and placed above the stirring mechanism of the hot plate and stirred for another 15 min at ambient temperatures.

The tube was permitted to stand until organic and aqueous layers were separated. The organic layer was transferred with a medicine dropper to a 2-dram vial and 2 ml of 0.1*N* NaOH was added. This mixture was quickly shaken by hand for 5 sec to remove excess H(tfa) from the organic layer. The two phases were immediately separated by withdrawing the organic layer with a medicine dropper and transferring it to another 2-dram vial which was then capped. This step must be performed rapidly and reproducibly because intolerably large amounts of Be will otherwise be lost and both precision and accuracy will suffer.

Five 1- μ l aliquots of organic layer were repetitively in-

jected into the gas chromatograph. The mean of peak heights from the Be(tfa)₂ peaks in the unknown solutions were compared with the average from five analyses of a standard solution of Be(tfa)₂. Over the concentration range studied the response is essentially linear so quantitation is simplified and peak height ratios can be used for the calculation of Be found.

Instrument Conditions. Gas chromatograph: Hewlett Packard Model 402 high efficiency gas chromatograph equipped with a ³H source electron-capture detector. Column: 2 m \times 3 mm i.d. borosilicate glass column packed with 2.8% W-98 silicone (Union Carbide) on Diatapore S (Hewlett Packard). Carrier Gas: CH₄, 10%; Ar, 90%; 54.5 ml/min. Column temp: 110°C. Detector temp: 200°C. On-column injection (no additional heat at site of injection).

Analysis for Blank. Periodic investigations were made to determine whether any interfering peaks, resulting from impurities or the reaction of reagents, coincided with the same retention time of Be(tfa)₂. Exactly the same analytical procedure and reagents in the analysis of unknowns were used. Deionized water containing aqua regia reagent was used in lieu of the unknown filter digest. The data obtained for 1 μ l of organic layer at an electrometer setting of range 10, attenuation 32, indicated peak heights of 5 mm which corresponds to a blank of <4% of Be found in typical unknowns or <0.00002 μ g Be/m³. In further experiments, an unused glass filter was subjected to aqua regia treatment and the resulting aqueous solution was analyzed. Here again, the blank was calculated to be less than 4% of the Be found in typical air sample determinations.

Recovery Studies. Recovery studies were made by using the above described procedure to determine the amount of beryllium in aqueous solutions made up to have concentrations similar to those of the unknown air filter digest samples. Five repetitive measurements were made on each of five independently prepared organic extracts, and the data in Table I were obtained.

Results and Discussion

Fourteen individual filter digests were analyzed by the gc procedure described. Five individual gc analyses were made for each sample to obtain a statistical mean, as well as five analyses of the standard beryllium solution of Be(tfa)₂. Figure 1 is a chromatogram of an air filter digest analysis for beryllium. Figure 2 is a chromatogram of a standard solution of Be(tfa)₂ (1.0×10^{-11} g Be/ μ l).

A precision study was performed in which the aqueous digest of one filter was carried through the analytical procedure five times to determine the precision of measurement of beryllium in a typical authentic filter. Table II is a tabulation of data obtained from these analyses.

The data obtained during the analyses of 14 typical urban

Table I. Beryllium Recovered from Known Aqueous Solutions

Mean error = 0.4×10^{-9}	
Relative error = 4.3%	
Concn in known aq soln, g/ml	Beryllium found, g/ml
9.2×10^{-9}	9.1×10^{-9}
	8.8×10^{-9}
	7.9×10^{-9}
	8.8×10^{-9}
	9.4×10^{-9}
	Mean 8.8×10^{-9}

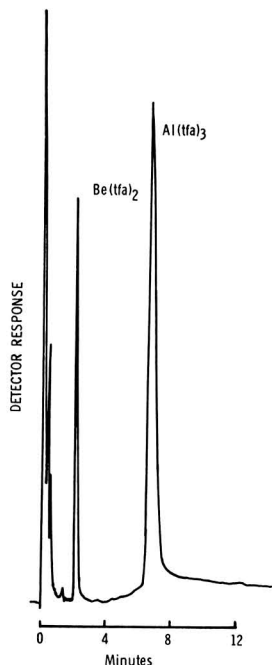


Figure 1. Chromatogram of beryllium extracted as $\text{Be}(\text{tfa})_2$ from an air filter digest solution, $0.00043 \mu\text{g Be/m}^3$; $1 \mu\text{l}$ sample injected

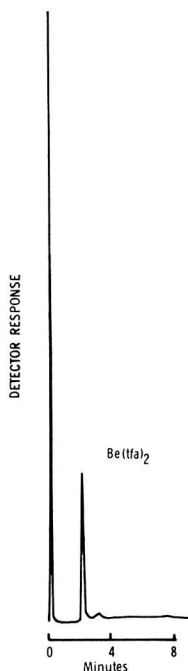


Figure 2. Chromatogram of $1 \mu\text{l}$ of a standard solution of $\text{Be}(\text{tfa})_2$ $1.0 \times 10^{-11} \text{g Be}/\mu\text{l}$

Table II. Beryllium Found in Air Filter Digest Precision Study

Relative standard deviation = 3.0%

Amount detected, g Be/ml aqueous digest	Amount detected, $\mu\text{g Be/m}^3$ air
2.3×10^{-8a}	4.1×10^{-4}
2.4×10^{-8}	4.3×10^{-4}
2.3×10^{-8}	4.1×10^{-4}
2.4×10^{-8}	4.3×10^{-4}
2.4×10^{-8}	4.3×10^{-4}
Mean 2.4×10^{-8}	

^a Mean of five gc injections compared with five gc analyses of standard.

air filter digest samples are listed in Table III. Our values fall within the range reported by Blosser and Thompson (1971), who analyzed samples by spark source mass spectrography.

Interferences. Although several metals were known to be present in these samples at much higher concentrations than the beryllium—e.g., Fe, 3.19; Pb, 6.0; Ni, 0.01; Cu, 0.61; and Mg, $0.13 \mu\text{g/m}^3$ in one urban sample analyzed by atomic absorption by Thompson et al. (1970)—the presently described gc method avoids these potential interferences. In the first step of the analytical procedure EDTA is used to remove most of several of the metals present as major constituents. Most of the remaining metals were removed rapidly by the sodium hydroxide backwash step. Any other remaining metals were removed or separated by the chromatographic column so that they did not interfere. The small amounts of aluminum and chromium that remained are indicated by two peaks eluting as $\text{Al}(\text{tfa})_3$ and $\text{Cr}(\text{tfa})_3$ at much longer retention times than that of the $\text{Be}(\text{tfa})_2$.

Sensitivity of Method. In this investigation it was not necessary to take full advantage of the extraordinary sensitivity of the gc method. Since the limit of detection has been determined to be about $4 \times 10^{-14} \text{g}$ of beryllium (Sievers et al., 1971), it should be possible to determine concentrations of beryllium lower by two orders of magnitude. In much lower concentration ranges, steps may have to be taken to reduce the blank.

Confirmation of the Identity of Eluted $\text{Be}(\text{tfa})_2$ by Gc–Ms. A critical limitation of the electron-capture detector is the

Table III. Beryllium Found in Air Filter Digest Samples

Sample no.	Amount detected, g Be/ml of aqueous digest	$\mu\text{g Be/m}^3$ of air
1	2.4×10^{-8}	0.00043
2	2.0×10^{-8}	0.00036
3	2.7×10^{-8}	0.00049
4	2.5×10^{-8}	0.00045
5	1.1×10^{-8}	0.00020
6	2.4×10^{-8}	0.00043
7	2.0×10^{-8}	0.00036
8	1.7×10^{-8}	0.00031
9	1.4×10^{-8}	0.00025
10	2.1×10^{-8}	0.00038
11	1.5×10^{-8}	0.00027
12	2.5×10^{-8}	0.00045
13	1.9×10^{-8}	0.00034
14	0.9×10^{-8}	0.00016

fact that this method of detection is so sensitive that in earlier studies, no qualitative method could be used to confirm unequivocally the identity of the eluting compound. Indirect methods have been used, such as tagging compounds with radioactive isotopes (Ross and Sievers, 1968; Ross et al., 1970) and cross-checking elution times on different types of chromatographic columns. Hughes et al. (1971) have recently developed an extremely sensitive gc-mass spectrographic system that will detect compounds eluting directly from the chromatograph at ultratrace levels—e.g., 10^{-11} g of metal (Wolf et al., 1972).

A standard $\text{Be}(\text{tfa})_2$ sample was analyzed by conventional scanning methods and m/e peak positions and intensities were determined. An appropriate peak is selected by the sensitivity of its detection and freedom from interferences arising from the solvent. The mass spectrometer detector is fixed on this mass peak and the compound of interest is separated and eluted from the chromatographic column and enters into the mass spectrometer. A single mass chromatogram of the selected compound fragment is obtained. This method was used to confirm the identity of the peak as $\text{Be}(\text{tfa})_2$. An independent measurement of the concentration of the Be in the air filter digest was made by gc-mass spectrometry and this compared very well with the measurement using an electron-capture detector. For the same filter digest, the concentrations were determined to be 2.5×10^{-8} g Be/ml digest by gc-mass spectrometry and 2.4×10^{-8} g Be/ml digest by gc with an electron-capture detector.

Conclusion

The method of analysis for beryllium by this gc method is very sensitive, and beryllium can be measured in air accurately and with good precision at levels two orders of magnitude below the AEC-recommended neighborhood maximum allowable concentration, $0.01 \mu\text{g Be}/\text{m}^3$ air (Tepper et al., 1961). The technique is relatively rapid, requiring about 30 min for the extraction procedure and less than 10 min for one gc analysis. The analysis can be performed on a relatively inexpensive analytical chromatograph. The method should be applicable for routine analysis of air and water samples

for beryllium to monitor trends and variations or for spot checks where beryllium is suspected to be close to or exceed the maximum allowable concentration. Variations of the method can be used for monitoring biological samples from persons suspected of exposure to dangerous concentration levels of beryllium.

Acknowledgment

We are indebted to Richard Thompson, Richard Enrione, and Larry Purdue of the Air Pollution Control Office for the samples used in this investigation and also to Mason Hughes and Michael Taylor of the Aerospace Research Laboratories for their mass spectrometric analyses.

Literature Cited

- Blosser, E. R., Thompson, R. J., Pittsburgh Conference on Analytical and Applied Spectroscopy, February 28–March 5, 1971.
- Moshier, R. W., Sievers, R. E., "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, England, 1965.
- Noweir, M. H., Cholak, J., ENVIRON. SCI. TECHNOL. 3, 927 (1969).
- Ross, W. D., Scribner, W. G., Sievers, R. E., "Analysis for Sub-Nanogram Amounts of Cobalt by Chelation and Electron Capture Gas Chromatography," proceedings of Eighth International Symposium on Gas Chromatography, Dublin, Ireland, September 1970.
- Ross, W. D., Sievers, R. E., *Talanta* 15, 87 (1968).
- Sievers, R. E., Eisentraut, K. J., Griest, D. G., Richardson, M. F., Wolf, W. R., Ross, W. D., Frew, N. M., Eisenhour, T. L., proceedings of 1971 Lunar Science Conference, Houston, Tex., January 1971.
- Taylor, M. L., Arnold, E. G., Sievers, R. E., *Anal. Lett.* 1 (12), 735 (1968).
- Tepper, L. B., Hardy, H. L., Chamberlin, R. I., "Toxicity of Beryllium Compounds," p 156, Elsevier, Amsterdam, The Netherlands, 1961.
- Thompson, R. J., Morgan, G. B., Purdue, L. J., *At. Absorpt. Newslett.* 9, 53 (1970).
- Wolf, W. R., Taylor, M. L., Hughes, B. M., Tiernan, T. O., Sievers, R. E., *Anal. Chem.* in press, 1972.

Received for review May 28, 1971. Accepted August 5, 1971. Research was sponsored by the Aerospace Research Laboratories, AFSC, U. S. Air Force, Contract No. F33615-69-C-1062

Mercury Inhibition on Lipid Biosynthesis in Freshwater Algae

Robert S. Matson, George E. Mustoe, and S. B. Chang¹

Department of Chemistry and College of Environmental Science, Western Washington State College, Bellingham, Wash. 98225

■ Mercuric chloride and methyl mercuric chloride inhibited the biosynthesis of lipids, especially galactolipids and chlorophylls in photosynthetically grown freshwater algae, *Ankistrodesmus braunii* and *Euglena gracilis*. Three and one-half parts per million of mercuric chloride gave 50% inhibition of galactolipid biosynthesis, 98% inhibition of chlorophyll synthesis in *A. braunii*, and a slightly smaller degree of inhibition in *E. gracilis*. Also, 2 ppm of methyl mercuric chloride caused 85% inhibition of galactolipid biosynthesis and 98% inhibition of chlorophyll biosynthesis in *A. braunii*. Both mercuric chloride and methyl mercuric chloride strongly inhibited the galactosyl transferase activity for the galactolipid biosynthesis in the chloroplasts isolated from *Euglena* cells and spinach leaves.

Toxic effects of mercury compounds in animals, including human beings, have been well documented (Kurland, 1971). Among several mercury compounds present in nature as pollutants, methyl mercuric chloride is known to be the most persistent and potent chemical species in various animal systems (Clarkson, 1971). The conversion of inorganic mercuric chloride to methyl mercuric chloride by microbial action has been reported (Jensen and Jernelov, 1969), although the mechanism of the conversion has not been established. The inhibition of the sulfhydryl enzyme activities by mercuric ion is a well-known phenomenon in biochemistry, and the toxic effect of mercury compounds in biological sys-

¹ To whom correspondence should be addressed.

tems may have been derived from the fact that the mercury element binds with the thiol group of the crucial enzyme proteins. Although the contamination of our aquatic environment with mercury has been reported, the biological effect of mercury compounds on unicellular algae, one of the important members in the aquatic food chain, has not been studied. The purpose of this paper is to discuss the results obtained from the study of the *in vivo* effect of mercuric chloride and methylmercuric chloride on the freshwater algae, *Ankistrodesmus braunii* and *Euglena gracilis*, under laboratory culture conditions and also the effects of these mercury compounds on an enzyme, galactosyl transferase, which is responsible for the biosynthesis of galactolipids, one of the major chloroplast lipids (Benson, 1963).

Experimental

ALGAE CULTURE. Stock cultures of *A. braunii* and *E. gracilis* were obtained from the Culture Collection, Department of Botany, Indiana University, Bloomington, Ind. About 10 ml of sterilized inorganic culture medium in a 50-ml flask was inoculated with cells from the stock cultures. The small culture was grown at 25°C under constant illumination (3 banks of fluorescence lamps) in an air-CO₂ (95:5%) atmosphere. About five days after the inoculation, the culture was transferred aseptically to 250 ml of the same type of medium in a 500-ml flask and incubation continued under the identical conditions. *A. braunii* cells were grown on an inorganic medium of Gaffron (1963) and harvested in a week. *E. gracilis* cells were grown on an inorganic medium of Cramer and Myers (1952) and harvested in a week to 10 days. Centrifuging the cultures for 5 min at 1000 *g* achieved harvesting.

Chemical Analyses. **CHLOROPHYLLS.** Chlorophylls were analyzed by the method of Arnon (1949).

GALACTOLIPIDS. Total galactolipid analyses were carried out by the method of Dubois et al. (1956). In this method, the galactose liberated by the acid hydrolysis of the galactolipids was determined colorimetrically.

TOTAL LIPIDS. Total lipids referred to the substance extracted with a solvent system of chloroform-methanol (2:1, v/v).

Enzymatic Assays. **ISOLATION OF CHLOROPLASTS.** Washed *Euglena* cells were suspended in 0.1M tris-HCl buffer, pH 7.3, to make a total volume of about 10 ml. The suspension was sonicated for 5 min in a sonifier (Branson Instruments, Inc., Stamford, Conn.) at the maximum power setting to break the cells. The sonicated sample was centrifuged at 1000 *g* for 5 min to remove unbroken cells and cell debris. Then, the supernatant was centrifuged at 5000 *g* for 10 min to sediment the chloroplasts.

ENZYMATIC REACTIONS. *Euglena* chloroplasts equivalent to 1-2 mg chlorophyll in 0.5 ml were incubated with 0.1 ml of UDP-[¹⁴C] galactose (U) (10,000 cpm) and 0.4 ml of 0.1M tris-HCl buffer, pH 7.3 at 37°C for 1 hr with constant shaking (Chang and Kulkarni, 1970). The reaction was stopped and the lipid products were extracted according to the method of Lennarz and Talamo (1966). At the end of the incubation time, the reaction was stopped by adding 4 ml of CHCl₃-MeOH (2:1, v/v) to the reaction mixture in 12-ml centrifuge tubes. The tubes were mixed on a Vortex mixer for a minute and placed in a 55°C water bath for 3 min. They were mixed again and returned to the bath for an additional 7 min. Then the tubes were taken out of the bath and were mixed again before the reaction mixtures were filtered through glass-wool to remove denatured proteins. The tubes and funnels were rinsed with 2 ml of CHCl₃-MeOH, and 2.5 ml of 0.9% aqueous NaCl was added to the filtrate. The mixture

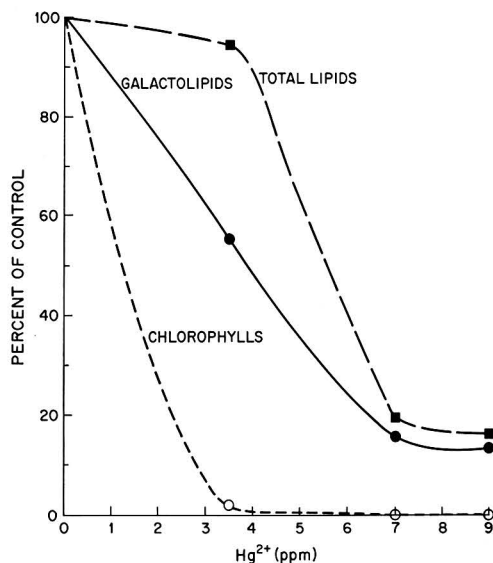


Figure 1. Effect of Hg²⁺ on lipid biosynthesis in *A. braunii*

was mixed well for 1 min and was chilled in an ice bath for 5 min. After centrifugation for 5 min, the upper aqueous layer was removed by a siphon, and the lower CHCl₃ layer was washed three more times with 2.5 ml each of distilled water. An appropriate aliquot (1 ml) of the CHCl₃ layer was transferred to a planchet, dried, and counted by a gas-flow counter (Nuclear Chicago, Chicago, Ill.).

Results and Discussion

IN VIVO STUDIES. When some freshwater algae were grown in the presence of mercuric chloride or methylmercuric chloride, chlorophyll synthesis and galactolipid synthesis were

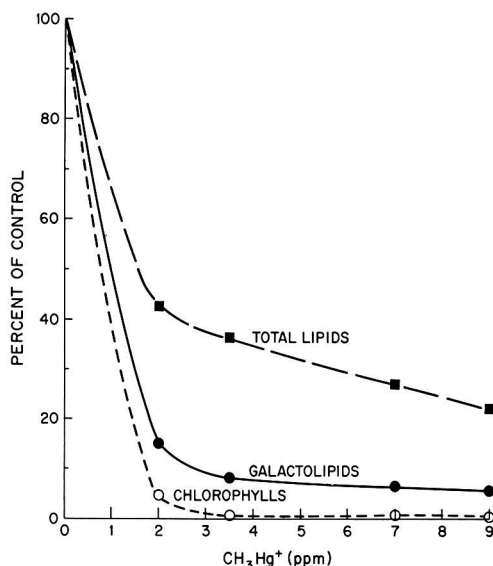


Figure 2. Effect of CH₃Hg⁺ on lipid biosynthesis in *A. braunii*

Table I. Effect of Cations on the Synthesis of Galactolipids

Ion added, 10 $\mu\text{mol/ml}$	MG, ^a cpm ^b	GD, ^c cpm	Total galacto- lipids, cpm
None	8,000	2,500	10,100
Mg ²⁺	7,700	2,460	10,000
Ca ²⁺	7,900	2,490	10,050
Mn ²⁺	5,200	1,600	6,500
Co ²⁺	1,000	320	1,200
Hg ²⁺	—	—	320
Na ⁺	7,000	2,000	8,700
K ⁺	7,500	2,200	9,400

^a Monogalactosyl diglyceride.

^b Counts per minute.

^c Digalactosyl diglyceride.

Table II. Inhibition of Mercury Ions on Galactosyl Transferase Activity in *Euglena* Chloroplasts^a

Tube no.	Hg ²⁺ , $\mu\text{mol/ml}$	CH ₃ Hg ⁺ , $\mu\text{mol/ml}$	Total galacto- lipids, cpm ^b
1	0	0	2,512
2	0.1	0	2,532
3	0.5	0	1,540
4	0.6	0	1,020
5	0.8	0	484
6	1.0	0	156
7	0	0.1	2,528
8	0	0.5	300
9	0	0.6	200
10	0	0.8	164
11	0	1.0	236

^a Each tube contained chloroplast equivalent to 0.85 mg, chlorophylls.

^b Counts per minute.

severely inhibited. Figure 1 shows that chlorophyll synthesis was almost completely (98%) inhibited and galactolipid synthesis was inhibited about 50% in *A. braunii* when mercuric chloride concentration was about 3.5 ppm. Actually, the significant inhibition of chlorophyll and galactolipid syntheses started when the mercuric chloride level was below 1 ppm. The effect of methyl mercuric chloride was even greater. As shown in Figure 2, a 2-ppm level of methyl mercuric chloride inhibited 98% of chlorophyll synthesis and 85% of galactolipid synthesis. The greater inhibitory effect of methyl mercuric chloride compared with that observed of inorganic mercuric chloride may result from the fact that methyl mercuric chloride, being somewhat less polar, may have better permeation through the membrane lipid region to get access to the target molecules, enzymes.

IN VITRO STUDIES. The chloroplasts isolated from the photo-synthetically grown *E. gracilis* cells have been shown to have high galactosyl transferase activity (Chang and Lin, 1971). This enzyme is involved in the synthesis of galactolipids, the major chloroplast lipids. Table I shows that mercuric ion (Hg²⁺) inhibited the galactosyl transferase activity more than any other cations studied. The mercuric ion inhibition is likely due to the binding of the ion with the thiol group in the enzyme protein (Chang, 1970). Table II shows the relative inhibitory effect of inorganic mercuric ion and methyl mercuric ion on the galactosyl transferase activity. As in the case of in vivo studies described in the previous section, the methyl mercuric ion had significantly greater inhibitory effect than the inorganic mercuric ion had. The difference in the inhibitory effect, again, may be due to the difference in the permeability through the chloroplast membrane between the inorganic mercuric ion and methyl mercuric ion.

Conclusion

The present investigation clearly indicates that mercuric chloride and methyl mercuric chloride strongly inhibit the syntheses of chlorophylls and galactolipids in whole cells of unicellular algae, *A. braunii* and *E. gracilis*, under photo-synthetic conditions. The mercury compounds also specifically inhibit the galactosyl transferase activity in *Euglena* chloroplasts. Since these mercury compounds inhibit strongly the syntheses of the important chloroplast components—i.e., chlorophylls and galactolipids—the similar detrimental effect could be expected to be true with other photosynthetic organisms including phytoplanktons and other species of unicellular algae.

Literature Cited

- Arnon, D. I., *Plant Physiol.* **24**, 1 (1949).
 Benson, A. A., National Academy of Science, Publication no. 1145, 571 (1963).
 Chang, S. B., *Phytochemistry* **9**, 1947 (1970).
 Chang, S. B., Kulkarni, N. D., *ibid.*, 927 (1970).
 Chang, S. B., Lin, M. F., *ibid.*, **10** (7), 1543-9 (1971).
 Clarkson, T. W., Abstract of the symposium "Mercury in the Western Environment," Portland, Ore. (1971).
 Cramer, M., Myers, J., *Arch. Mikrobiol.* **17**, 384 (1952).
 Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., Smith, F., *Anal. Chem.* **28**, 350 (1956).
 Gaffron, H., Florida State University, Tallahassee, Fla., private communication, 1963.
 Jensen, S., Jernelov, A., *Nature* **223**, 753 (1969).
 Kurland, L. T., Abstract of the symposium "Mercury in the Western Environment," Portland, Ore. (1971).
 Lennarz, W. J., Talamo, B., *J. Biol. Chem.* **241**, 2707 (1966).

Received for review March 17, 1971. Accepted June 25, 1971.
 A part of this investigation was supported by grants from the National Science Foundation (GB-23045) and National Institute of Health (AP-01152-02 Public Health).

Biopolymers of Activated Sludge

Lowell L. Wallen¹ and Edwin N. Davis

Northern Regional Research Laboratory, Peoria, Ill. 61604

■ Activated sludge from the municipal sewage treatment plant at Peoria, Ill. was extracted with hot water and organic solvents. Heteropolysaccharides and a polyester were obtained by water and chloroform extraction, respectively. Bacterial strains have been isolated from activated sludge. Some of these bacteria produced polysaccharides when grown on 0.5% glycerol or glucose. An acquired strain of *Zoogloea ramigera* produced a heteropolysaccharide from glucose. Photomicrographs of extracted and unextracted activated sludge indicate that polymeric material is removed by extraction with hot water.

Municipal sewage has been treated for many years by aerobic biological systems that oxidize organic waste to water, carbon dioxide, and low-molecular-weight water-soluble compounds. Two methods of treatment are common today—the trickling filter and the activated sludge process. In the latter, clarification of sewage water by activated sludge is accomplished by rapid flocculation of the biomass, followed by entrapment and subsequent settling. We are investigating activated sludge to gain a better understanding of its composition and properties and to exploit potential possibilities for its commercial utilization.

Studies by Tenney and Stumm (1965) indicate that polysaccharides are a major factor in the physical behavior characteristics of the sludge. Crabtree et al. (1965, 1966) believe that poly- β -hydroxybutyrate is implicated in the process; whereas Tezuka (1969) theorized that metallic cations could be bound to the negatively charged surfaces of microbial cells to form a bridge between them and thus cause flocculation to occur.

Friedman et al. (1968) isolated an organism from sewage and identified it as *Zoogloea ramigera*. It is presumed to be a predominant species in sewage. Capsular material surrounding the cells was a fibrillar polymer that contained only glucose and resembled cellulose, having β -1,4 linkages. It was slightly soluble in water but had properties of a polyelectrolyte with increased solubility in alkaline solutions.

Anderson and McCoy (1963) obtained bacterial isolates from activated sludge that produced polysaccharide material when grown on a 0.2% glycerol-salt-phosphate medium. A pentose and hexosamine were identified as components of the polysaccharide. These same components were also found in hydrolyzed extracts from natural sludge flocs.

Nishikawa and Kuriyama (1968) reported the separation of a polysaccharide mixture and deoxyribonucleic acid (DNA) from sewage-activated sludge by extraction with 0.5M sodium carbonate. These products were also extracted readily by water

if the sludge was first extracted with acetone; however, the products were not easily obtained if the acetone extraction was eliminated.

We have examined activated sludge taken from several locations in the municipal sewage treatment facility at Peoria, Ill. The sludge contains polymeric material that is being investigated as to its physical and chemical properties. Bacteria have also been isolated from these sewage samples, and some have demonstrated the ability to produce polysaccharides. Dias and Bhat (1964) isolated more than 300 microbial strains from activated sludge and found *Zoogloea* and *Comamonas* species to be predominant. However, only the former genus produced flocs from autoclaved sewage which resembled those from activated sludge.

Procedure

Microbiological Isolations and Acquisitions. Aerated sewage samples were collected in sterile plastic jugs at the Peoria plant. One-milliliter samples of activated sludge were added to 20 ml of 0.05% arginine medium (Crabtree et al., 1965) containing biotin, folic acid, and cobalamin, but no penicillin. These mixtures were incubated for 20 hr at 28°C on a Gump rotary shaker at 200 rpm. About 200 colonies were obtained from a 10⁶ dilution prepared from these samples. Isolates were grown for 48 hr at 28°C in 50 ml of arginine medium containing 0.5% glucose. One of our isolates, a g-neg rod (NRRL B-3793) from a re-aeration tank, produced a polymer that has been investigated. Eight pure cultures of bacterial sewage isolates designated as *Z. ramigera* were secured from several outside sources. They varied both in growth and polymer-producing characteristics.

Sludge Extraction. Samples of aerated sewage from the Peoria Sanitary District plant were allowed to settle for 1–2 hr. The settled sludge was centrifuged at 4000 \times g for 30 min and was stored at –22°C until used. Wet sludge was extracted in the extracting medium of choice with heating when desirable. Aqueous extracts of polysaccharides were prepared either from sludge that had been extracted previously with one or more organic solvents or from unextracted sludge. Such extracts were made with boiling water or with alkaline solutions at room temperature. Crude products were precipitated by adding a threefold (v/v) excess of ethanol. In a few preparations, a four- or fivefold excess volume was used.

Organic nonpolysaccharide substances and water were removed simultaneously from wet sludge by azeotropic distillation with benzene. The volume of water removed was measured and the benzene extract evaporated to give a black viscous mixture of unknown composition.

Polysaccharide Degradation. Polymers were hydrolyzed either with 2N or 6N hydrochloric acid in a sealed tube immersed in boiling water for 1–3 hr or heated in an autoclave for 3 hr at 15 psi; alternatively, they were refluxed overnight in 2N sulfuric acid. Oxidation reactions with sodium metaperiodate were done by the procedures of Rankin and Jeanes (1954).

¹ To whom correspondence should be addressed.

Paper Chromatography. Chromatograms of hydrolyzates were prepared by descending irrigation with *n*-butanol-pyridine-water (6:4:3) for 16 hr on Whatman No. 1 paper. Spots were visualized by either silver nitrate, aniline hydrogen phthalate, or ninhydrin.

Gas Chromatography. Dried hydrolyzate samples were converted to their trimethylsilyl derivatives by the method of Sweeley et al. (1963). Derivatives were chromatographed on a 4-ft column of 3% SE-52 on Chromosorb W (80/100 mesh) at a programmed temperature range of 155–270°C (20°/min).

Scanning Electron Microscopy. Electron micrographs were prepared on a Cambridge Stereoscan electron microscope at magnifications up to 20,000. Samples were coated with aluminum by vacuum deposition before viewing.

Infrared Spectra. Spectra were prepared from the solid state by internal reflection spectroscopy. Samples were applied to the surface of a KRS-5 plate (Wilks Scientific Corp., South Norwalk, Conn.) by evaporation of a solution of the material being examined.

Viscosity Determinations. Viscosity was determined at four concentrations (0.45, 0.60, 0.73, 0.85%) of polymer with a Brookfield viscometer, type LVF, at spindle speeds of 6, 12, 30, and 60 rpm and at temperatures of 10°, 25°, 40°, and 55°C.

Experimental

Polymer from Activated Sludge. A sample of wet sludge weighing 813 grams, from the exit end of the reeration tanks of the Peoria plant, was extracted with boiling benzene until no more water was removed by azeotropic distillation. The dry residual sludge was a powdery material (107 grams), which had lost nearly 80% of its original wet weight as water and an additional 1.8% as benzene-extractable substances. One hundred grams was subsequently extracted with 1200 ml of boiling water for 15 min. The water extract was a clear amber-colored solution after centrifugation at 10,400 × *g* for 30 min. It was concentrated in vacuo to one fourth its original volume and product recovered by addition of ethanol (4:1 v/v). The crude material when dried weighed 4.85 grams. A 2-gram portion was dissolved in 80 ml distilled water and centrifuged at 20,400 × *g* for 10 min. Addition of ethanol (5:1) gave 1.1 grams of a light tan product (dry weight), representing an overall yield of 2.7 grams of purified product from 100 grams dry extracted sludge.

Hydrolysis of this product in an autoclave with 6*N* HCl for 3 hr (sealed tube) and subsequent gas chromatography of the trimethylsilylated derivatives showed peaks for glucose, mannose, rhamnose, and possibly galactose and xylose. Integration of peak heights indicated that 41% is glucose, 13% is mannose, and 20% is rhamnose. Paper chromatography of the hydrolyzate gave spots for glucose, mannose, rhamnose, galactose, a hexosamine, maltose, and lactose. The hexosamine was visualized by ninhydrin; it moved just behind glucose, a position which could indicate it to be glucosamine or galactosamine.

A solution of polymer from sludge was treated for 4 hr at pH 4.5 and 45°C with cellulase from *Aspergillus niger* (Sigma, pract. grade, Type I). The free glucose detected was indicative of β-1,4 bonded glucose molecules in the structure.

Activated sludge polymer precipitates from alcohol were flocculant but nonadhesive, and aqueous solutions of these polymers were less viscous than those prepared with polymers from *Z. ramigera*. The latter produced polymers whose

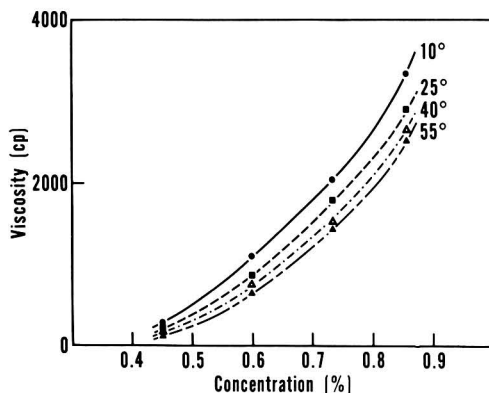


Figure 1. Viscosity of NRRL B-3669 polymer as a function of temperature and concentration

solutions were thick and gelatinous, and when polymer was precipitated with ethanol, it adhered to a glass rod.

Polymer from Sewage Bacterial Isolate. Isolate NRRL B-3793 produced an alcohol precipitable polymer when shaken at 25°C for 72 hr in 0.5% Casitone, 0.1% yeast extract, and 0.5% glycerol. The organism also produced polymer in lesser amounts when either glucose or ethanol was used as a substrate. Polymer yields and production were erratic, usually ranging from 3 to 5.5%, but at times, none was formed. Gas and paper chromatography of acid hydrolyzates showed rhamnose and mannose to be present, and possibly galactose. One experiment gave a product containing only mannose as a major component.

Polymer from Acquired Organisms. An organism acquired by our ARS Culture Collection, designated as *Z. ramigera* NRRL B-3669M, produced a water-soluble polysaccharide from 0.5% glucose, 0.5% Casitone, and 0.1% yeast extract medium in 55–74% yields (gram polymer/100 grams glucose). This polymer was hydrolyzed by 2*N* HCl for 1 hr in a capped (sealed) tube immersed in boiling water. Gas and paper chromatography of the hydrolyzate showed glucose, mannose, and galactose to be present. No color was observed with addition of iodine to a solution of the unhydrolyzed polymer.

The product was also oxidized by sodium metaperiodate (Rankin and Jeanes, 1954). Reduction with sodium borohydride and subsequent acid hydrolysis of the periodate-oxidized polymer gave a mixture containing formic acid and intact hexose molecules identified as glucose, mannose, and galactose. These results indicated that the polymer contained 1,3 and 1,6 linkages. In addition, glycerol and either threitol or erythritol were found. The presence of the 4-carbon sugar alcohols is evidence for 1,4 bonds, while glycerol is formed in the reaction sequence from the presence of either 1,2 or 1,6 links in the original polymer. The amount of unused periodate in the reaction mixture showed that 1,3 bonds are present in approximately 40% of the polymer, and 1,6 bonds make up 21% of the total.

When the polymer was incubated with cellulase at 45°C in 0.1*M* phosphate-citrate buffer at pH 4.5 for 2 hr, no definite evidence for glucose formation was found; thus no β-1,4 bonds were present between glucose molecules in a form susceptible to attack by cellulase.

A 0.85% solution of polymer from organism NRRL B-3669 was prepared by solubilizing the material in distilled water for 1 min with a Waring Blendor, followed by stirring

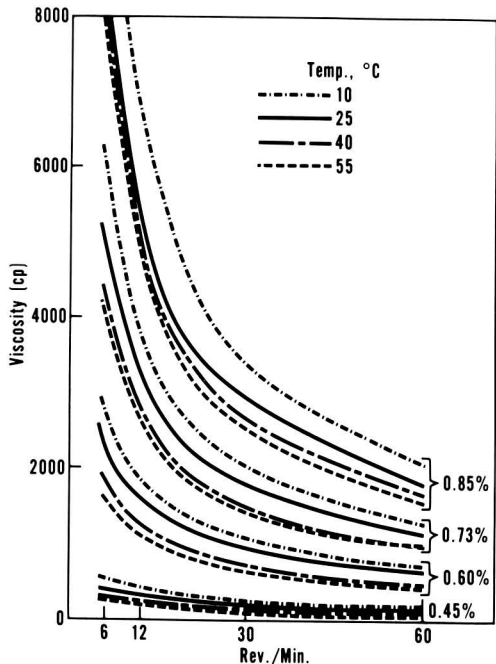


Figure 2. Viscosity of NRRL B-3669 polymer as a function of concentration, temperature, and shear

at room temperature for 65 hr. The Brookfield viscosity was determined to be 2972 cP at 25°C with a spindle speed of 30 rpm. Data for various concentrations and temperatures are plotted in Figures 1 and 2.

Figure 1 shows that the viscosity of the B-3669 polymer varies inversely with temperature. At lower concentrations, there was little viscosity change with increasing shear (Figure 2), but at higher concentrations, there was a rapid initial reduction in viscosity under these conditions, regardless of temperature.

Polyester. A polyester was obtained in 1.3% yield from chloroform extracts of dried activated sludge by addition of ethyl ether (3:1 v/v) and subsequent chilling. The flaky product was separated into two fractions with hot ethanol. Ethanol-insoluble material melted at 169–170°C and gave an infrared spectrum like those published for polyhydroxybutyrate (Haynes et al., 1958). The alcohol-soluble product precipitated when chilled and melted at 100–105°C. It contains β -hydroxybutyric acid but has a different structure than poly- β -hydroxybutyrate. This product predominates over poly- β -hydroxybutyrate in activated sludge and is a new product not reported previously. Work is being done on its composition and structure.

Discussion

Although little is known of the composition of activated sludge, it is one of the most abundant intermediate products produced in sewage treatment plants. The large number of microorganisms present in sewage makes it quite obvious that polysaccharides should be formed, as the microbial production of such compounds is a common occurrence. Although microbial oxidation with activated sludge is a mixed culture operation, it was stated by Dias and Bhat (1964),

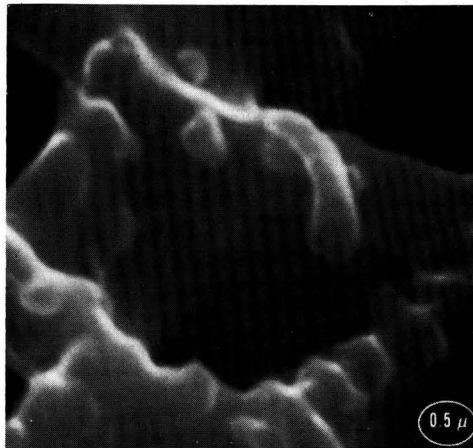


Figure 3. Electron micrograph of dry activated sludge before extraction with hot water, 20,000 \times

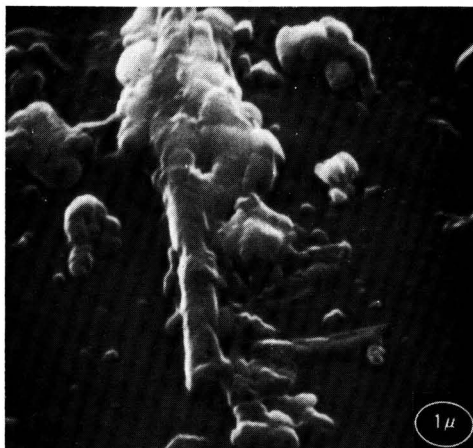


Figure 4. Electron micrograph of activated sludge after extraction with hot water, 10,000 \times

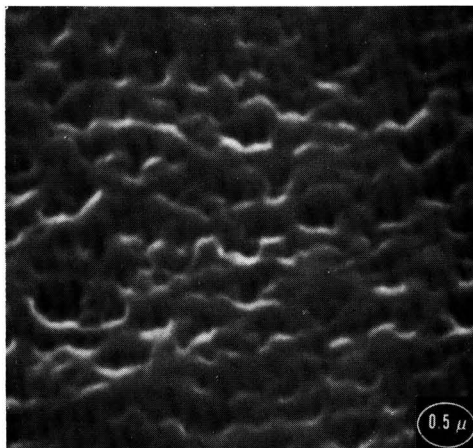


Figure 5. Electron micrograph of polymeric material extracted from dry activated sludge by hot water, 20,000 \times

among others, that *Zoogloea* and *Comamonas* species appear to predominate. One of our acquired strains of *Z. ramigera* produced a polymer whose solutions had a viscosity comparable with those of other microbial polysaccharides, yet possessed properties and composition different from the product reported by Friedman et al. (1968).

Our g-neg sewage isolate (NRRL B-3793), although somewhat erratic in its polymer production, produced yet another type of polymer. Although structural studies are not complete, this polymer has no glucose in its structure, and the organism produces less polymer when glycerol is replaced by glucose as a carbon source. These examples demonstrate the potential for variety in the polysaccharide content of activated sludge. Results from our studies of polymeric material separated from benzene-extracted sludge indicate that it contains a mixture of polysaccharides. Such a mixture is not unlikely in view of the variety of microbial species present in aerated sewage treatment tanks.

Electron photomicrographs were prepared from an activated sludge sample prior to extraction with boiling water and also after extraction. The product derived from hot water extraction was reprecipitated from 1N sodium hydroxide with ethanol (3 v/v). Scanning electron micrographs of the non-extracted and extracted sludge, as well as of the product, are reproduced in Figures 3-5, respectively. Figure 3 shows what is believed to be a mass of polymeric material in which microbial cells are embedded. The view of extracted sludge (Figure 4) shows residual polymer with cells; Figure 5 portrays the surface of material precipitated from the extract and reprecipitated as described.

These photomicrographs support the beliefs of Tenney and Stumm (1965) and of Friedman et al. (1968) who implicate polysaccharides as a major factor in the behavior characteristics of activated sludge. Extraction with hot water changed the appearance of the sludge and gave an alcohol-precipitable product which appears different from unextracted sludge in

that no microbial cells are present (compare Figures 3 and 5).

The production of polysaccharides and of a new polyester by microorganisms of activated sludge indicate that quantities of such materials could become available from the large amounts of sludge available. Activated sludge would appear to be a source of other products in addition to those reported here. It is possible that such products may have commercial value which would assist in underwriting the cost of sludge disposal.

Acknowledgment

We thank F. L. Baker for his preparation of the scanning electron photomicrographs.

Literature Cited

- Anderson, R., McCoy, E., *Bacteriol. Proc.*, p 162 (1963).
Crabtree, K., Boyle, W., McCoy, E., Rohlich, G., *J. Water Pollut. Contr. Fed.*, **38**, 1968-80 (1966).
Crabtree, K., McCoy, E., Boyle, W., Rohlich, G., *Appl. Microbiol.*, **13**, 218-26 (1965).
Dias, F., Bhat, J., *ibid.*, **12**, 412-17 (1964).
Friedman, B., Dugan, P., Pfister, R., Ramsen, C., *J. Bacteriol.*, **96**, 2144-53 (1968).
Haynes, W. C., Melvin, E. H., Locke, J. M., Glass, C. A., Senti, F. R., *Appl. Microbiol.*, **6**, 298-304 (1958).
Nishikawa, S., Kuriyama, M., *J. Ferment. Technol.*, **46**, 381-6 (1968).
Rankin, C., Jeanes, A., *J. Amer. Chem. Soc.*, **76**, 4435-44 (1954).
Sweeley, C. C., Bentley, R., Makita, M., Wells, W. W., *ibid.*, **85**, 2497-2507 (1963).
Tenney, M., Stumm, W., *J. Water Pollut. Contr. Fed.*, **37**, 1370-88 (1965).
Tezuka, Y., *Appl. Microbiol.*, **17**, 222-6 (1969).

Received for review September 30, 1970. Accepted July 8, 1971. Presented at the 160th ACS Meeting, Chicago, Ill., September 1970. This is a laboratory of the Northern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture. The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

Bromine and Chlorine Loss from Lead Halide Automobile Exhaust Particulates

John A. Robbins¹

Great Lakes Research Division

Franklin L. Snitz

Department of Environmental and Industrial Health, University of Michigan, Ann Arbor, Mich. 48104

Most lead in the atmosphere, especially in urban areas, originates from combustion of gasoline containing alkyl lead antiknock compounds (Middleton, 1971). Commonly used antiknock mixtures contain ethylene dibromide and ethylene dichloride which react with lead in the engine combustion chamber to form lead halide particles that are emitted in the exhaust.

Recent measurements of halogens and lead in aerosols in Cambridge, Mass. by Lininger et al. (1966) and in Fairbanks, Alaska by Winchester et al. (1967) indicate that a considerable proportion of bromine in urban air may originate from ex-

haust emissions. Their data suggest further that particulate lead halides undergo loss of bromine in the atmosphere. Some direct evidence for such loss was obtained by Loucks and Winchester (1969) who sampled, at selected time intervals, auto exhaust introduced into a closed garage and found an order of magnitude decrease in the Br/Cl ratio over a 40-min time interval.

The reasons for the change in halogen composition are not well understood, but historical evidence on the photosensitivity of lead halide compounds which darken on exposure to sunlight (Sunyal and Dhar, 1923) suggests a photochemical release mechanism. Pierrard (1969a) observed both bromine and chlorine loss in the presence of uv radiation from powdered

¹ To whom correspondence should be addressed.

■ Fresh automobile exhaust particulate matter introduced into a 10-m³ transparent, outdoor enclosure has been analyzed for bromine and chlorine by neutron activation analysis and for lead electrochemically. Particles in the equivalent diameter range of about 0.05 to 2 μ were collected at selected time intervals on a filter preceded by a two-stage Andersen impactor to eliminate large particles. The measured Cl/Pb ratio showed a slow ($t_{1/2} \sim 4$ hr) exponential decrease in time while the Br/Pb ratio decreased much more rapidly ($t_{1/2} \sim 15$ min) during the first 30 min. A comparison of dark vs. sunlight runs

shows no difference in the rates of change of composition and indicates that the mechanism for selective loss of Br relative to Cl is not primarily photochemical. A quantitative model is developed which assumes that the loss rate is determined by the rate of outward diffusion of halide ions to particle surfaces where they are efficiently volatilized. Although the model satisfactorily accounts for present observations, additional information is required to distinguish among several alternative loss mechanisms leading to roughly the same dependence of loss rate on particle size.

lead halide samples. Although his results were interpreted as indicating a photochemical dependence, they are inconclusive on this point since the variation of the rates with light intensity was apparently not studied.

The present experiment was undertaken to determine with precision the rate of loss of bromine and chlorine from exhaust particulate matter and whether the rate is affected by the presence of sunlight.

Experimental

An enclosure of approximately 10 m³ volume was constructed outdoors by covering a 5 × 8 × 10 ft wooden frame with 4-mil (0.01-cm) polyethylene sheet. A 6-in. slit in one wall served as a port for introducing exhaust particulate matter and for sampling.

Polyethylene was determined by uv spectrophotometry to be a suitable wall material for this experiment. As can be seen from Figure 1, the transmission is essentially constant at wavelengths greater than about 300 nm which is approximately the short wavelength cut off for ground level solar radiation (General Motors Research Laboratories, 1962; Korth, 1966). Thus, the relative spectral intensity distribution of sunlight is largely unaltered by the wall. The absolute transmissivity is larger than indicated in the figure because the somewhat cloudy plastic sheet scatters light out of the collimated beam of the spectrophotometer. Since exhaust emissions condensed on the polyethylene could potentially alter its transmission characteristics, the measurement was repeated on a portion of wall ex-

posed during the reported runs. No significant change was observed.

The sampling system consisted of a two-stage (stages 1 and 3) Andersen (1966) impactor placed roughly at the center of the enclosure and attached by a 1-meter length of 1-cm i.d. polyethylene tubing to a filter assembly outside which was in turn connected to a Gelman twin-cylinder high-vacuum pump (Model NO). The filter housing could easily be removed from the line via quick disconnect joints permitting rapid substitution of new filters in their individual assemblies during the first few exposures made in rapid succession. Only the 25-mm diam Whatman No. 41 cellulose fiber filters were analyzed. The impactor itself served merely to eliminate particles with aerodynamic diameters greater than about 2 μ. Thus large "spurious" halogen or lead-rich particles, such as those which might be derived from entrained soil as well as exhaust system deposits of re-entrained or flaked particles with diameters above 200 μ (Habibi et al., 1970) were not collected. Use of the impactor stages as a prefilter facilitated collection of freshly generated particulate matter.

The Whatman 41 filters are quite suitable for the present experiment since they permit high flow rate (54 l./min) with adequate retentivity and low analytical blank values for Cl, Br, and Pb. System blanks for each element, obtained by sampling the enclosure air for about a 10-min interval prior to introduction of exhaust were 100- to 1000-fold lower than the content of filters exposed to exhaust. The collection efficiency of the prefilter-filter system is indicated as the dashed curve in

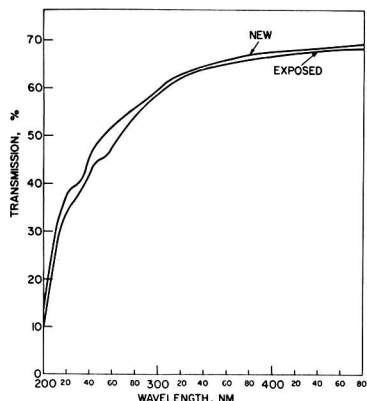


Figure 1. Transmission characteristics of polyethylene film before and after use as the enclosure wall

Passage of ground level solar radiation through the wall does not significantly change its spectral distribution in the wavelength region of interest

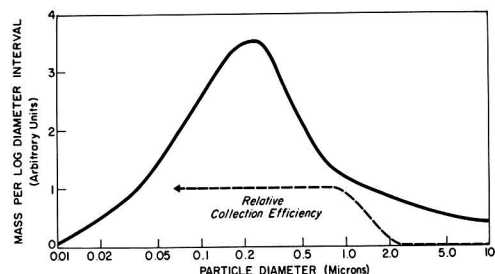


Figure 2. The Pb differential mass distribution vs. effective particle diameter derived from the cumulative mass distribution in Cincinnati air measured by Flesch (1969)

Dashed curve indicates the apparent collection efficiency of the filter arrangement of this experiment. Between 0.08 and 1 μ, the efficiency is essentially 100%

Table I. Composition of TEL Motor Mix (Ethyl Fluid)*

Compound	Wt %
Tetraethyllead (TEL)	61.48
Ethylene dibromide	17.86
Ethylene dichloride	18.81
2,6-di- <i>tert</i> -Butylphenol	0.3
Orange dye	0.0621
Inerts	1.49
	100.0

* Analysis of mix used in the present experiment obtained from Ethyl Corp.

Figure 2 where the upper cut off is due to the impactor and the lower cut off is uncertain. According to measurements of Lindeken et al. (1963), the collection efficiency should be essentially 100% down to 0.08- μ diam at the present estimated airflow velocity of 250 cm/sec and may remain high into lower size ranges, although no observations are presently available below 0.08 μ . Also presented in Figure 2 is a differential Pb mass distribution inferred from the cumulative distribution reported by Flesch (1969) for Cincinnati air. While this distribution may be typical of aged Pb particulate matter, it is nevertheless suggestive of the mass distribution for the present experiment. It will be seen that the region where the efficiency is expected to be 100% brackets the broad maximum in the Pb distribution. Roughly 80% of the total emitted Pb is collected on the filter.

Exhaust particulate matter was generated by an automobile burning leaded gasoline to which an additional 10 ml/gal of TEL motor mix was added (Table I). The car (1967 Dodge 273 in.³ engine) was preconditioned by driving it for a half an hour at 60 mph and then leaving it to run at a fast idle near the enclosure. A 2-meter section of approximately 20-cm i.d. flexible stainless steel tube was attached to the exhaust pipe with a heat-resistant silicon rubber sleeve and allowed to adjust to the passage of hot exhaust gases for a half hour prior to the beginning of a run. At the onset of a given run, the end of the stainless steel tube was inserted into the enclosure for about

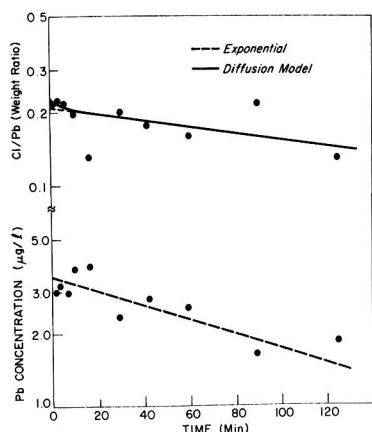


Figure 3. The absolute lead concentration in $\mu\text{g/l}$. and the chlorine-to-lead ratio vs. elapsed time in minutes for a dark run using TEL-enriched gasoline

Both sets of data show an approximately exponential decrease; $t_{1/2}$ for Cl/Pb is about 4 hr. Uncertainties in the Pb concentrations are about 20% and in Cl/Pb ratios about 25%

20 sec displacing 10–20% of the air so that the portion of exhaust introduced into the enclosure represented fresh particulate matter generated under reproducible steady-state conditions. Particulate sampling began immediately after withdrawal of the tube for a number of selected time intervals covering a total observation period of several hours.

As each exposure was completed, the filters were packaged in 8-ml polyethylene vials and stored at Dry-Ice temperature until they could be analyzed for bromine and chlorine a few hours after the end of the entire run. All filters had a yellowish-brown "tobacco stain" coloration and a faint odor characteristic of mixed degraded hydrocarbons.

The nondestructive neutron activation analysis procedure for many trace elements including bromine and chlorine is described in detail elsewhere (Dams et al., 1970). The polyethylene vial containing the filter and a similar vial containing a Whatman 41 filter on which a standard solution of KBr and KCl was deposited were pneumatically positioned in a "rabbit" alongside the core of the University of Michigan nuclear reactor for 5 min in a neutron flux of approximately 2×10^{12} n/cm²/sec. At 4 min after irradiation, the sample was counted for 400-sec live time using a 30-cm³ Ge(Li) detector coupled to a Nuclear Data 4096 channel pulse height analyzer, and the standard was then counted for 400 sec in the same geometry. (Because of the comparable amounts of Br and Cl on the filter, the 620-KeV Cl double escape interference with the 617-KeV Br photopeak is negligible.) With a correction applied for decay of the standard during the sample counting, a comparison of net peak areas at 617 KeV and 1642 KeV yielded absolute mass of Br and Cl on the sample filter. Uncertainties in the absolute weights of Br and Cl are about 15% while uncertainties in the Br/Cl ratio are about 5%. Non-destructive analysis is particularly suitable in the present experiment, because it is necessary to study the effect of filter storage on the Br/Cl ratio. If Br is lost relative to Cl prior to collection, there is certainly a possibility that further loss might occur in collected aerosols during storage of the filter. Re-analysis of filters stored for several days at Dry-Ice temperatures, however, showed no significant change in the absolute halogen contents.

Neutron activation analysis is not suitable for the deter-

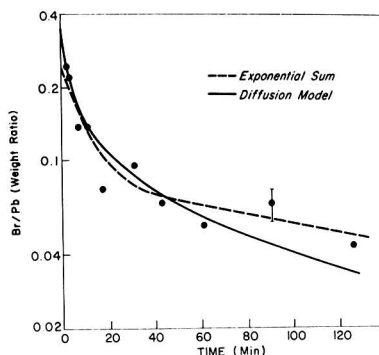


Figure 4. The bromine-to-lead ratio vs. elapsed time for the same run as in Figure 3

The data are approximated by a sum of two exponentials (dashed line fit) with $t_{1/2}$ (short) = 15 min and $t_{1/2}$ (long) = 4 hr. The model fit (solid curve) extrapolates at $t = 0$ to 0.39 in agreement with the expected value. Individual ratios are uncertain by about 25%

mination of lead. For lead analysis, the previously irradiated and counted filters were soaked in dilute nitric acid for several weeks to ensure complete leaching of lead from the filters. The solution, adjusted to 10-ml volume, was then analyzed both by atomic absorption spectrophotometry and by anodic stripping voltammetry (Allen et al., 1970). A comparison of results of the two techniques indicates an uncertainty of about 20% in the absolute weight of lead.

Results

The results of a dark run at ambient temperature of 20°C are shown in Figures 3 and 4. Exhaust was introduced into the enclosure at night when the only apparent light sources were a few incandescent and fluorescent lights glowing within distant buildings. The exponential drop in absolute Pb concentration to half its initial value in 2 hr is probably, in large measure, due to leakage associated with the pumping action of the flexible walls that respond easily to slight breezes.

The Cl/Pb ratio also decreases exponentially with a half-life of about 4 hr. This dependence is described empirically by the straight line drawn in Figure 3 where

$$\frac{\text{Cl}}{\text{Pb}} = \alpha e^{-\lambda_1 t} \quad (1)$$

with $\alpha = 0.21 \pm 0.02$ and $\lambda_1 = 0.003 \pm 0.002 \text{ min}^{-1}$ obtained from a least-squares fit.

The time dependence of the Br/Pb ratio, shown in Figure 4, is approximated by a function of the form

$$\frac{\text{Br}}{\text{Pb}} = \beta e^{-\lambda_2 t} + \gamma e^{-\lambda_3 t} \quad (2)$$

where best fit, shown as the dashed line, is for $\beta = 0.17 \pm 0.03$, $\gamma = 0.08 \pm 0.01$, $\lambda_2 = 0.08 \pm 0.02 \text{ min}^{-1}$, and $\lambda_3 = 0.002 \pm 0.001 \text{ min}^{-1}$. Initially bromine decreases relative to lead at a much greater rate than does Cl, but after approximately 1 hr, the rate of decrease of each relative to lead is the same within experimental errors ($\lambda_1 = \lambda_3$).

This can be best seen in Figure 5 where the statistical uncertainties in the Br/Cl ratio are much less than for the ratio of the halogens to lead. The fit, indicated by the dashed line, is obtained from the function

$$\frac{\text{Br}}{\text{Cl}} = \delta e^{-\lambda t} + K \quad (3)$$

where $\delta = 0.80 \pm 0.09$, $K = 0.31 \pm 0.03$, and $\lambda = 0.056 \pm 0.007 \text{ min}^{-1}$. In principle, $\lambda = \lambda_2 - \lambda_1$, but λ is better determined than λ_2 .

Also presented in Figure 5 are the results, indicated by (+), of a daytime run at an ambient temperature of 15°C. Exhaust was introduced in the morning when the sun was illuminating the entire enclosure. There is no significant difference in the time dependence of the Br/Cl ratio between night and day runs. In addition to these two runs using TEL-enriched gasoline, a dark run using regular leaded gasoline was performed. The two points (Δ) from this run shown in Figure 5 indicate agreement in the Br/Cl time dependence with the other runs.

Discussion

According to Habibi et al. (1970), the major lead salt in 2- to 10- μ diam exhaust particulate matter is PbBrCl with 2PbBrCl·NH₄Cl present only as a minor constituent, while submicron particles are primarily 2PbBrCl·NH₄Cl. Thus, the expected values of the Cl/Pb weight ratio for these size classes are 0.17 and 0.25, respectively. Extrapolation of Equation 1 to

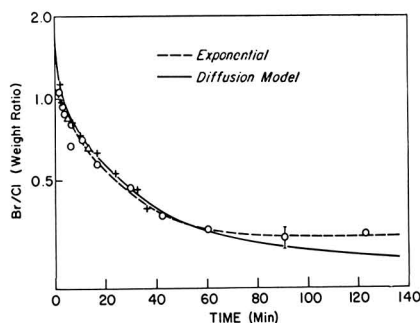


Figure 5. The bromine-to-chlorine ratio vs. elapsed time for dark and daylight runs

(Dark runs: \circ , TEL-enriched gasoline; Δ , regular leaded gasoline. Full sunlight run: +, TEL-enriched gasoline) The data are approximated by an exponential decrease superimposed on a constant minimum. $t_{1/2} = 15 \text{ min}$ (dashed line). The model fit (solid curve) underestimates the actual values at times larger than an hour by up to 15%. Individual ratios are uncertain by about 5%

$t = 0$ (fresh particulate matter) gives a Cl/Pb ratio of 0.21 ± 0.02 suggesting an admixture of roughly 75% 2PbBrCl·NH₄Cl and 25% PbBrCl, provided, of course, these are the only chlorine and lead compounds in the exhaust particulate matter. According to Habibi's observations, an admixture of PbBrCl is expected in the present samples since some particles with diameters above 1 μ were collected on the filter in addition to those of submicron size. Thus it is reasonable to assume that the bromine as well as lead and chlorine are primarily in the two chemical forms above so that the Br/Pb weight ratio is independent of particle size and equal to 0.39. However, extrapolation of Equation 2 to $t = 0$ gives a Br/Pb weight ratio of 0.25 ± 0.03 which is significantly lower. One possible reason for this low observed value is that Equation 2 does not correctly represent a rapid initial loss of bromine. If the actual $t = 0$ value is 0.39, then roughly 20% of the total bromine must have left the particulate phase within the first 30 sec, since the earliest measurement which was initiated at about 15 sec elapsed time for a duration of 1 min gave a Br/Pb ratio of 0.24.

To see the possibility of developing a quantitative model to reconcile the above facts, we consider a specific rate-limiting mechanism where bromide ions in the particles diffuse outward in a concentration gradient established by reactions leading to loss at the surface. Exhaust particulate matter introduced into the enclosure is further treated as a system of noninteracting lead halide spheres initially identical and uniform in composition with a time-independent size distribution.

Pierrard (1969b) advanced the idea originating with Kittel (1966) of a photolytic mechanism with three major steps: (1) creation and trapping of ions and electrons at lattice sites, (2) diffusion of atoms or holes away from these sites, and (3) loss of reaction products at the surface. In the present model, photons play no explicit role, so that the factor of effective radiation intensity does not enter a mathematical expression for halogen loss as it does in Pierrard's work (1969b). Instead, the rate is assumed to be limited by the mobility of Br⁻ ions in the lattice (step 2), and the surface is treated as a perfect sink for volatilization so that the Br⁻ concentration at the surface is taken as being negligibly small. Specific reactions leading to bromine loss are not considered in this formalism which follows an approach developed earlier for halogen exchange in marine

aerosols (Robbins, 1970). If D_{Br} is the diffusion constant for Br ions in solid lead halide, the total amount of Br contained in a spherical particle of radius, R , after elapsed time, t , can be shown to be (Jost, 1952):

$$M_{Br}(R,t) = M_{Br}(R,0) \cdot F(R,t) \quad (4)$$

where

$$F(R,t) = \frac{6}{\pi^2} \sum_{\nu=1}^{\infty} \frac{1}{\nu^2} e^{-\nu^2 \pi^2 D t / R^2} \quad (5)$$

and $M_{Br}(R,0)$ is the initial amount of bromine [$F(R,0) = 1$].

To relate Equation 4 to the mass collected on the filter, it is necessary to know the particle mass distribution. Unfortunately, it is not known in the present experiment, and such data are difficult to obtain. However, the results of Flesch (1969) may be used as an approximation in developing a model keeping in mind that the reported lead mass distribution for downtown Cincinnati air may be only qualitatively similar to the one unobserved in the present experiment. If the lead mass per unit log radius interval shown in Figure 2 is written as $dM_{Pb}/d(\ln R)$, it can be seen that the mass of bromine per unit log radius interval after elapsed time, t , is given by

$$\frac{dM_{Br}(t)}{d(\ln R)} = k_{Br} \cdot \frac{dM_{Pb}}{d(\ln R)} \cdot F(R,t) \quad (6)$$

while the Br/Pb weight ratio of particles collected on the filter is given by

$$\frac{Br}{Pb} = k_{Br} \frac{\int_{-\infty}^{+\infty} \frac{dM_{Pb}}{d(\ln R)} \cdot \epsilon(R) \cdot F(R,t) d(\ln R)}{\int_{-\infty}^{+\infty} \frac{dM_{Pb}}{d(\ln R)} \cdot \epsilon(R) d(\ln R)} \quad (7)$$

where $\epsilon(R)$ is the collection efficiency indicated in Figure 2, and k_{Br} is the value of the Br/Pb ratio at $t = 0$.

A computer program was written to find the values of D_{Br} and k_{Br} which give the best agreement of Equation 7 with the data in the least-squares sense. The result for Br/Pb ratio is indicated as the solid curve in Figure 4 with $D_{Br} = (8 \pm 1) \times 10^{-15} \text{ cm}^2/\text{sec}$ and $k_{Br} = 0.39 \pm 0.05$. The exact agreement of k_{Br} with the expected result is obviously fortuitous, but it is not an artifact of the model since both k_{Br} and D_{Br} were allowed to vary in the least-squares fit. According to the model, the rapid initial decrease in bromine appears to be due to the presence of very small lead halide particles which can quickly lose this halogen. The calculated time evolution of the bromine mass distribution is illustrated in Figure 6 where dM_{Br} -

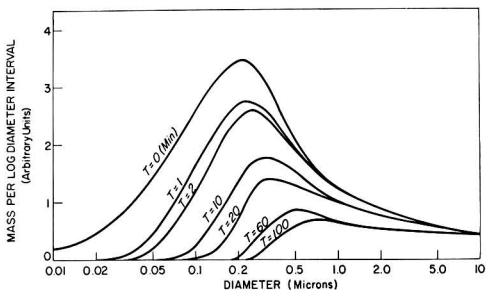


Figure 6. Time dependence of the bromine mass distribution according to the Br^- ion diffusion model

$D_{Br} = 8 \times 10^{-15} \text{ cm}^2/\text{sec}$. At $t = 0$, the distribution is assumed to be proportional to the lead distribution shown in Figure 2

(t)/ $d(\ln (2 R))$ is shown for different times, using the above value for D_{Br} . It can be seen that after only 2 min of aging, a $0.1\text{-}\mu$ particle has lost 50% of its initial bromine content. The two-parameter model fit of Equation 7 is not significantly worse than the four-parameter empirical fit of Equation 2, and the value of D_{Br} appears to be reasonable, falling at the low end of a range of values for ions in solids spanning many orders of magnitude (Jost, 1952). A measured value for this particular case is not readily available from the literature.

The model can also be applied to the Cl data, where results of the fit are indicated by the solid line in Figure 3. Departure from the dashed line obtained from Equation 1 occurs only for very fresh particulate matter where the fit appears to be slightly improved although statistically, the difference is small. Here, $D_{Cl} = 8 \times 10^{-17} \text{ cm}^2/\text{sec}$ and $k_{Cl} = 0.25$. According to the present model (a), the Cl is more tightly bound in the solid than the Br by two orders of magnitude, or (b) the particle surface may simply not be as effective a sink for chloride ions. The second alternative is expected if the sink mechanism is oxidation of the halide to the volatile element since at chemical equilibrium with oxidizing agents, Br_2 is evolved in preference to Cl_2 .

The formalism can be applied to the Br/Cl ratio independently. Using D_{Cl} obtained above, and varying D_{Br} and the initial Br/Cl ratio, k , the result is shown as the solid line in Figure 5 with $D_{Br} = 8 \times 10^{-15} \text{ cm}^2/\text{sec}$ as before and $k = 1.7$. The fit is excellent except for times greater than an hour for which the model underestimates amount of Br present by about 15% at 2 hr. The difference could, of course, well be due to the approximate mass distribution function used, but other reasons might include the development of a layer which inhibits further bromine loss, as could result from replacement of Br^- ions in the vicinity of the particle surface with oxides or attachment of hydrocarbons, etc. This last possibility may account for the apparent stability of the halogen content of the samples of particulate matter during collection and prior to analysis if loss is internally controlled since collected exhaust particles may be rapidly coated with hydrocarbons. The accretion on lead halide particle surfaces of substances which inhibit halogen loss may be a factor in the observed increase of the Br/Pb ratio in urban air with decreasing visibility (Lininger et al., 1966). Pierrard (1969a) suggests that more uv radiation from sunlight is available to initiate photochemical Br release during periods of high visibility while on the evidence of the present experiment, it seems more plausible that during such periods, there is less material in the atmosphere which can "poison" particle surfaces.

Much of the above discussion must remain speculative in the absence of a simultaneous measurement of the particle size distribution. The value of D_{Br} , in particular is sensitive to its form, while k_{Br} is not. If there were relatively fewer particles of small size than assumed here, the inferred value of D_{Br} would have to be larger to account for the observed loss rate since D_{Br} is very roughly proportional to the mean square particle radius for a particle size distribution of this general shape. While the value of D_{Br} depends mainly on the form of the particle size distribution, the shape of the curve describing the Br/Pb ratio vs. time is not sensitive to it. Its shape is primarily that of the function $F(R,t)$, that is

$$\frac{Br}{Pb} \sim k_{Br} F(\bar{R},t) \quad (8)$$

where \bar{R} is the rms radius of the particle size distribution. Equation 8 is strictly correct only if the size distribution is so narrow that it is replaceable by a delta function centered at $R =$

\bar{R} . The value of k_{B_1} depends to a large extent on the choice for $F(R,t)$.

Models in which loss is determined by the rate of diffusion to the surface of reactants—e.g., O_3 , NO_x —in the atmosphere surrounding the particle or by reactions at the particle surface lead to functional forms of $F(R,t)$ which are qualitatively similar (Robbins, 1970). Thus, additional experiments including measurement of the particle size distribution, especially for particles in the 0.01- to 0.1- μ diam range, need to be made to distinguish among alternative models.

Conclusions

Preliminary experiments indicate that bromine and chlorine are lost relative to lead in particulate matter present in fresh automobile exhaust from combustion of leaded gasoline. The loss rate for bromine is much greater than for chlorine during the first half hour, and the rate is apparently not affected by the presence or absence of sunlight during this time. The measured loss rates may be accounted for quantitatively by assuming outward diffusion of halide ions to particle surfaces where they are volatilized. With additional information, especially simultaneous particle size distribution measurements alternative models could be examined using techniques developed in this work.

Acknowledgment

The authors are particularly indebted to J. W. Winchester for his support and thoughtful criticism of this work. We wish to thank L. F. Gilbert and C. F. Gordon of the Ethyl Corporation for the donation of the ethyl fluid and Sherman Funk of the Willow Run Laboratory, Motor Vehicle Compliance Section for use of the exhaust coupling equipment. Acknowledgment is also due Ronald Lininger and William Pierson for their expressions of interest, and Lawrence Hecker for his assistance in the lead measurements.

COMMUNICATION

Filtration of Ferric Hydroxide

Gordon A. Lewandowski¹ and Henry B. Linford

Department of Chemical Engineering, Columbia University, New York, N.Y. 10027

■ Optimum conditions for ferric hydroxide filtration were sought by measuring the surface charge of the particles as well as by obtaining direct filtration data. Streaming potential measurements were used as a means of indicating the relative surface charge, and this data correlated well with filtration rates. That is, maximum rates occurred at the same pH as zero surface charge. Optimum conditions of filtration were pH 6.6, high iron concentration, and the use of NaOH or KOH rather than calcium hydroxide as the precipitating base. Agitation and rate of base addition did not appear to significantly affect filterability within the range of the experimental conditions.

Literature Cited

- Allen, H. E., Matson, W. R., Mancy, K. H., *J. Water Pollut. Control Fed.*, **42**, 573-81 (1970).
Andersen, A. A., *Amer. Ind. Hyg. Ass. J.*, **27**, 160-5 (1966).
Dams, R., Robbins, J. A., Rahn, K. A., Winchester, J. W., *Anal. Chem.*, **42**, 861-7 (1970).
Flesch, J. P., *J. Colloid Interface Sci.*, **29**, 502-9 (1969).
General Motors Research Laboratories, *Search*, 1962.
Habibi, K., Jacobs, E. S., Kunz, W. G., Pustell, D. L., "Characterization and Control of Gaseous and Particulate Exhaust Emissions from Vehicles," Presentation at the Air Pollution Control Association Fifth Technical Meeting, San Francisco, Calif., October 8-9, 1970.
Jost, W., "Diffusion in Solids, Liquids and Gases," Academic Press, New York, N.Y., 1952, pp 45-6.
Kittel, C., "Introduction to Solid State Physics," 3rd ed., Wiley, New York, N.Y., 1966, pp 512-21.
Korth, M., U.S. Public Health Service Publication No. 999-AP-20, 1966.
Lindeken, C. L., Morgin, R. L., Petrock, K. F., *Health Phys.*, **9**, 305-8 (1963).
Lininger, R. L., Duce, R. A., Winchester, J. W., Matson, W. R., *J. Geophys. Res.*, **71**, 2455-63 (1966).
Loucks, R. H., Winchester, J. W., "Trace Substances in Environmental Health III," Conference Proceedings, University of Missouri, June 1969, pp 233-50.
Middleton, J. T., *Amer. Sci.*, **59** (2), 188-94 (1971).
Pierrard, J. M., *ENVIRON. SCI. TECHNOL.*, **3**, 48-51 (1969a).
Pierrard, J. M., PhD Thesis, "Photolysis of Lead Halides," Dept. of Chemistry, University of Washington, Seattle, Wash., (1969b).
Robbins, J. A., "Precipitation Scavenging (1970)," A.E.C. Conference Proceedings, Richland, Wash., June 1970, pp 325-51.
Sunyal, A. K., Dhar, N. R., *Z. Anorg. Chem.*, **128**, 212-17 (1923).
Winchester, J. W., Zoller, W. H., Duce, R. A., Benson, C. S., *Atmos. Environ.*, **1**, 105-19 (1967).

Received for review April 30, 1971. Accepted August 20, 1971. This work was supported in part by the U.S. Atomic Energy Commission under contract AT(11-1)-1705 and by the U.S. Public Health Service under grant AP-00585.

Iron compounds are present in many industrial waste streams, and the removal of these compounds by a hydroxide precipitation would be most effective provided this material could be separated out of suspension by a reasonable filtration process. It was the object, therefore, of this investigation to improve the filtration rate of ferric hydroxide, and in this connection, five different variables were studied: final pH, type of base used, base addition rate, rate of agitation, and concentration of iron.

In order that a better understanding of the chemical and physical properties of the hydroxide precipitate might be

¹ Present address: FMC Corp., 500 Roosevelt Ave., Carteret, N.J. 07008. To whom correspondence should be addressed.

$$\zeta = \left(\frac{E_s}{\Delta P} \right) \lambda \left(\frac{4 \pi k \mu}{D} \right)$$

where E_s = streaming potential; ΔP = pressure drop across the bed; λ = conductivity of the filtrate; μ = viscosity of the filtrate; D = dielectric constant of the filtrate; and k = proportionality constant, $9 \times 10^9 \text{ n} \cdot \text{m}^2/\text{coulomb}^2$. This expression was used to correlate the streaming potential data.

Apparatus

Apparatus used was according to Lewandowski, 1970; Linford et al., 1968.

Detailed diagrams of the streaming cell and equipment are given in Figures 1 and 2. Silver-silver chloride electrodes were situated above and below the bed and then connected to a Keithley electrometer (Keithley Instruments, Cleveland, Ohio) with an impedance of 10^{14} ohms. With measured voltages of the order of 10^{-3} V, the streaming current was approximately 10^{-17} A. Therefore, polarization of the electrodes is negligible, and the measured potential difference is a true streaming potential. Furthermore, since the supporting electrolyte is more than $10^{-3}N$ in KCl, surface conduction is not a problem in this study.

Figure 3 describes the equipment used to study filtration time.

Procedure

Under agitation (135, 260, and 490 rpm), 500 cc of ferric chloride (0.02M and 0.2M) were placed in a 1000-cc graduated cylinder and 500 cc of KOH of sufficient concentration added to bring the pH of the filtrate to the desired level. The KOH was usually poured from a flask in about 15 sec (2000 cc/min); however, data is also presented for a KOH addition rate of 4 cc/min. Agitation was normally continued for 5 min after base addition to ensure complete homogeneity. Then, under 60-cm Hg vacuum, 116 cc of the suspension were transferred to the Millipore holder (Millipore Filter Corp., Bedford, Mass.), a clock was started, and the time recorded at each 2-cc interval of collected filtrate (measured in the vacuum breaker) until the liquid level fell below the surface of the bed. The filter paper was #934AH (Reeve Angel, Clifton, N.J.)

For the streaming potential measurements, the beds were formed on a disk of filter paper placed over the fritted disk

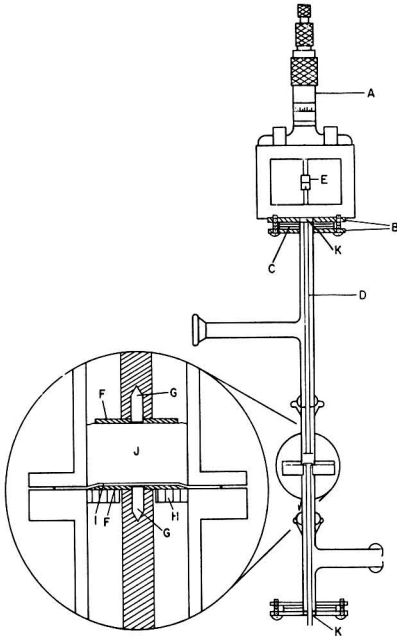


Figure 1. Streaming potential cell

A, Starrett micrometer depth gauge; B, aluminum flanges; C, rubber gaskets; D, silver rod; E, nylon connector; F, silver-silver chloride electrodes; G, silver pin; H, fritted glass disk; I, filter support; J, deposited bed; and K, O-rings

obtained, the formation of this precipitate was also studied from the point of view of surface chemistry. Because of the complex shape, wide size distribution, and high particle concentration, reliable electrophoretic mobility measurements are difficult, if not impossible, to obtain with ferric hydroxide suspensions. However, reliable streaming potential measurements can be obtained in the apparatus described here. A well-known expression (MacInnes, 1961) for the zeta potential, in terms of the streaming potential, is given as:

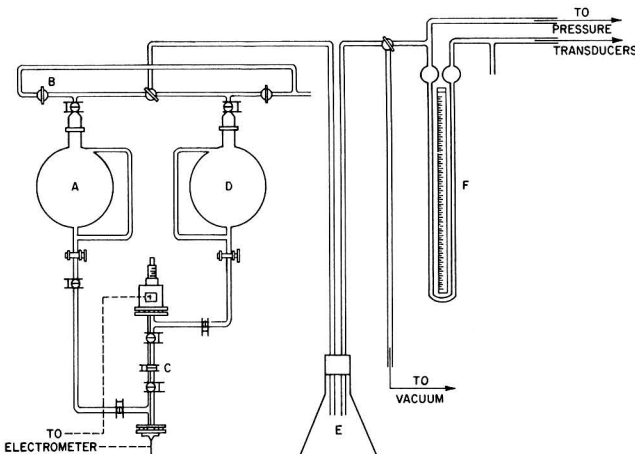


Figure 2. Streaming potential apparatus

A, D, 1-liter flasks; B, vacuum release valve; C, streaming cell; E, vacuum trap; and F, manometer

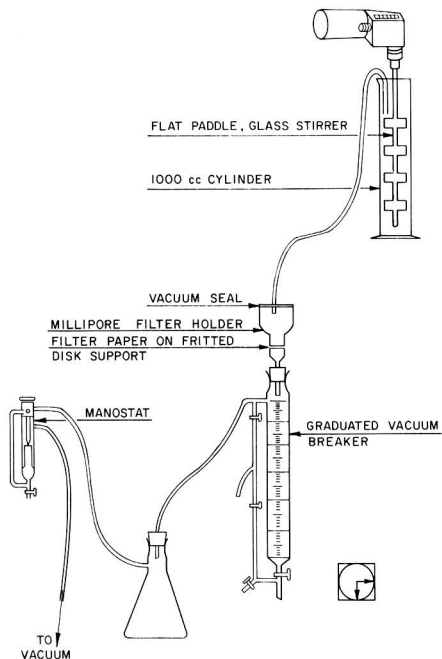


Figure 3. Filtration apparatus

surrounding the lower electrode (Figure 1), and then the upper and lower electrodes were joined in the streaming apparatus (Figure 2). A vacuum was drawn on flask A and then slowly released. The streaming potential was then recorded as a function of the pressure drop, and the zeta potential related to the slope by the above equation. Pressure transducers were used to measure the pressure drop, and E_s vs. ΔP was recorded automatically on an EAI Variplotter (Electronic Associates, Inc., Long Branch, N.J.).

The suspension preparation was altered for calcium hydroxide addition because of its partial solubility. In this case, a 500-cc suspension of calcium hydroxide was agitated for 5 min prior to addition of 500 cc of 0.02M ferric chloride. In all but two cases, the method of addition was simply to pour the reagent from a flask (approximately a 15-sec total addition time). However, the two exceptions were notable. In one, the ferric chloride was added dropwise at 11 cc/min (about a 45-min total addition time). This apparently allowed more time for reaction to take place and ensured complete solubility of the calcium hydroxide particles prior to filtration. The filtration time was decreased by about 18%. In the other case, 50 cc of 0.2M ferric chloride was poured into the calcium hydroxide suspension, and this mixture was agitated for 30 min (instead of the usual 5 min). Thereafter, the suspension was diluted up to 1000 cc and agitated for an additional 20 min prior to filtration. This reduced the filtration time about 68% down to a level commensurate with the KOH addition (Figure 4). The temperature for all runs was $25.5^\circ \pm 1.0^\circ\text{C}$.

Results and Discussion

The filtration results are summarized in Figure 4. Filtration times are for 100 cc of collected filtrate. The two sets of three curves each represent the mean and 90% confidence limits

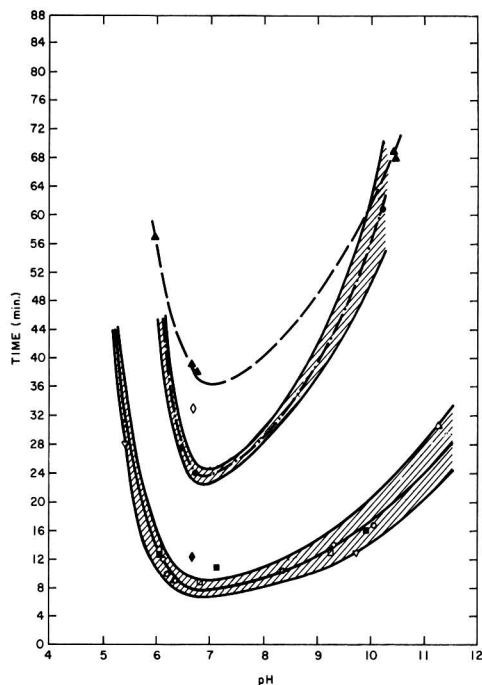


Figure 4. Filtration time

○ KOH added at 2000 cc/min to 0.02M FeCl_3 @ 260 rpm; □ @ 490 rpm; ■ @ 135 rpm; △ NaOH @ 260 rpm; ▽ KOH at 4 cc/min and 260 rpm; ● KOH added at 2000 cc/min to 0.2M FeCl_3 @ 260 rpm, solids content $10\times$ that in the other cases; ▲ 0.02M FeCl_3 added at 2000 cc/min to Ca(OH)_2 @ 260 rpm; ◆ 0.2M FeCl_3 ; and ◇ 0.02M FeCl_3 at 11 cc/min

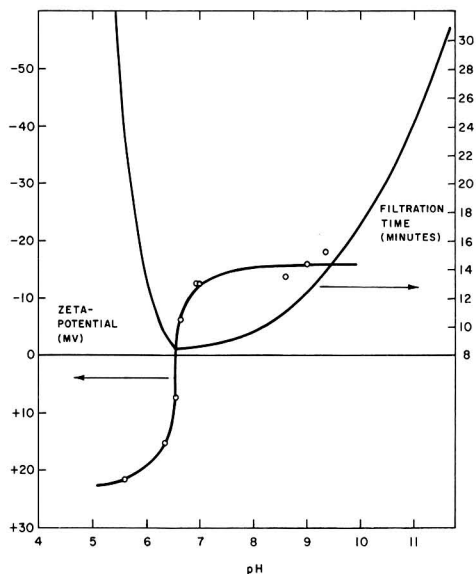


Figure 5. Zeta potential

when KOH was used as the precipitating base at low and high concentrations of iron.

The filtration results also show that, within the range of each variable, the rate of agitation and the rate of base addition have a negligible effect on the filtration time (except when calcium hydroxide is used), while control of the final pH of the filtrate is of the utmost importance, having an optimum in the range pH 6.5–7.5. Outside of this range, the filtration times (and therefore pumping costs or filter area requirements) increase quite rapidly, particularly on the acid side.

Increasing the iron concentration also appears to be beneficial from the point of view of filtration time per unit weight of filtered solids. This time improved threefold in going from 0.02M to 0.2M ferric chloride solutions (although the absolute filtration time was slower). However, any potential savings in filter area requirements (per unit weight of filtered solids) would have to be weighed against the additional capital or operating expenditure which may be required for concentrating the iron.

Finally, while use of sodium and potassium hydroxide exhibit similar filtration properties, use of calcium hydroxide results in a much slower filtration time (fourfold increase), unless proper precautions are taken with regard to iron concentration and agitation time to allow the calcium hydroxide particles to react with the ferric chloride and reach equilibrium. This implies increased holding time (under agitation) of the suspension and possibly a concentration of the iron as described above, and the added costs of such modifications would have to be weighed against the additional operating cost incurred by using KOH or NaOH as the precipitant.

The zeta-potential results are reported in Figure 5, which

describes a particle of ferric hydroxide that goes from a positive to a negative surface charge, with a zero point at pH 6.6. Furthermore, the shape of the zeta-potential curve indicates an adsorption phenomena at the particle surface, possibly involving several ferrihydroxyl complexes (Lewandowski, 1970; Parks and de Bruyn, 1962). The conditions of precipitation of the suspensions used in the zeta-potential study were: 260-rpm agitation, the KOH solution added to 0.02M ferric chloride by pouring the base from a flask (15-sec total addition time), and a temperature of 25.5°C. These conditions correspond approximately to ferric hydroxide suspensions in 0.03M KCl. Filtration data, under the same conditions, are plotted on the same graph as the zeta-potential curve. This indicates that a zero zeta potential corresponds to an optimum filtration rate, a result which is expected from coagulation theory (Kruyt, 1952).

Literature Cited

- Kruyt, H. R., Ed., "Colloid Science, Vol 1: Irreversible Systems," Chap. VI, pp 245-77, Elsevier, Amsterdam, Holland, 1952.
- Lewandowski, G., PhD thesis, Columbia University, New York, N.Y., 1970.
- Linford, H., Fyfe, R., Hilborn, W., Lausanggam, S., "Cationic Polymers as Flocculation Aids in Water Purification," Dept. of Interior, Federal Water Pollution Control Administration, Terminal Progress Report WP 00240-06, 1968.
- MacInnes, D. A., "The Principles of Electrochemistry," p 439, Dover, New York, N.Y., 1961.
- Parks, G. A., de Bruyn, P. L., *J. Phys. Chem.*, **66**, 967-73 (1962).

Received for review October 20, 1970. Accepted September 3, 1971.

CORRESPONDENCE

Attenuation of Power Station Plumes as Determined by Instrumented Aircraft

SIR: Stephens and McCaldin (1971), in their article entitled "Attenuation of Power Station Plumes as Determined by Instrumental Aircraft," [ES&T, **5** (7), 615 (1971)] present some interesting data on SO₂ and particle concentrations in plumes. They assume that the emitted particles with $d > 0.3 \mu\text{m}$ remain in the plume thus constituting a "conservative" or inert tracer so that SO₂ decay in the plume may be estimated. They then estimate:

- For relative humidities (RH) below 40%, there is little or no SO₂ decay.
- For RH in the range 40–55%, the SO₂ decay corresponds to a half-life of 140 min
- For 78–80% RH, the SO₂ decayed with a 70-min half-life.

In their discussion, the authors properly point out that their particle measurements might have been affected by the

humidity so that the findings are not confirmed. They hoped that they might solve the problem by using impactors or heating the particle sampler inlet directly.

I would like to point out an error in their assumption which is even more grave than the above problem, and, I believe, invalidates their findings with regard to SO₂ decay in power station plumes. It is well-known that atmospheric SO₂ is readily oxidized to sulfate in particulate form. I contend that enough SO₂ is converted to particulate matter in the plume so that the assumption of the particles as a conservative tracer is grossly in error. Consider an SO₂ concentration of 0.5 ppm or 1425 $\mu\text{g}/\text{m}^3$ STP. The conversion of 2% of this to sulfate particles with a density of 2 g/cm^3 will result in 110 particles/cm³ with diameter of 0.4 μm . (This of course neglects dilution by atmospheric dispersion.) This particle concentration is higher than any reported by the authors in Figure 6. What this calculation illustrates is that only a small fraction

of the SO_2 need be converted to particulate SO_4^{2-} to account for a large fraction of the particles measured by the authors. Furthermore, the rate of decay of SO_2 must therefore be considerably slower than estimated in the paper.

The SO_2 to SO_4^{2-} conversion by catalytic oxidation in solution (Junge and Ryan, 1958; Scott and Hobbs, 1967) is likely to be greater at high than at low relative humidities. The results of the paper seem to confirm this quite well.

As a final note it is pointed out that in stack plumes as well as in many urban atmospheres, the mass of sulfur in the form of sulfur dioxide is much larger than the mass of sulfur in

particulate sulfate. Nonetheless, sulfate comprises a large fraction of the particle mass.

Literature Cited

Junge, C. E., Ryan, T. G., *Quart. J. Roy. Meteorol. Soc.*, **84**, 46-56 (1958).
Scott, W. D., Hobbs, P. V., *J. Atmos. Sci.*, **24**, 54-7 (1967).

James P. Friend

*Department of Meteorology and Oceanography
New York University
University Heights
Bronx, N. Y. 10453*

SIR: With regard to the correspondence concerning our recent article, we would like to point out that the term SO_2 *decay* was used rather than *oxidation* to cover several possible mechanisms of SO_2 removal from the plume. It is quite possible, of course, that SO_2 may be absorbed or adsorbed on particulate matter, or it may go into solution in the presence of sufficient moisture, and/or it may certainly undergo heterogeneous or homogeneous oxidation processes. The question is, what is the probability that these potential SO_2 loss mechanisms will affect the numbers of particles larger than the size range measured and thus influence the particulate/ SO_2 ratio?

One of the more probable mechanisms of loss would be the catalyzed oxidation of SO_2 at one of the already established particulate surfaces. In our studies, particle counts were recorded for sizes greater than 0.3 or 0.5 μ diam. There are large numbers of particles in the size range below these values which were not counted, and which would also present surfaces for SO_2 reactions. Since it has been shown that further oxidation ceases at a pH of about 3, which would be achieved quite soon on a small particle surface in the absence of a neutralizing agent, we feel that this mechanism would not exert a major influence on the particulate/ SO_2 ratio. The effect of humidity on the particle count was, of course, acknowledged in the paper.

Inasmuch as there would be a distribution of SO_2 over all

sizes of particulate matter and the reaction most probably occurs at the surface of existing particles, the probability of the formation of new particles, and more important perhaps, the formation and growth of new particles to sizes larger than 0.3 and 0.5 μ which would have been counted would be of much less significance. It should be noted that plume age was a maximum of 4 hr.

It has been shown, of course, that gas-phase photochemical oxidation of SO_2 may produce sulfuric acid mist, although the rate of reaction is on the order of 0.1%/hr. If one considers that even this rate requires sunlight and that these studies were conducted just after sunrise in plumes formed and transported at night, then it seems likely that contributions to the particle population of a size large enough to be counted from this source would be of minor significance.

As previously pointed out, the technique is certainly not definitive, however we feel that the effort was not without merit, particularly in view of the corroborative nature of the results with data obtained by widely different techniques and the contributions it may have to future development of more precise procedures.

N. Thomas Stephens

*Air Pollution Research Laboratory
Department of Civil Engineering
Virginia Polytechnic Institute and
State University, Blacksburg, Va.*

industry trends

Ford Motor Co. has entered into contracts with Koppers Co., Inc., to reduce emissions at Ford's Rouge coke ovens. Contract calls for installation of automatic lid-lifters on openings where coal is fed to the ovens, and improvement of systems that control emissions during the coking cycle.

B. F. Goodrich Chemical Co. has started up operation of its \$450,000 Avon Lake waste water treatment systems. System will treat wastes from a general chemicals plant (making PVC and other plastics) and the Development Center which does process R&D.

General Electric is working with the TVA's Browns Ferry nuclear power plant to install advanced treatment systems for the plant's gaseous releases. TVA is aiming for a radiation dose of 3 mrem/year—far less than the normal background count of about 115 mrem/year.

Cincinnati Drum (Ludlow, Ky.) has been commended for its new air pollution controls by the Kentucky Air Pollution Control Commission. Cincinnati Drum recycles and reconditions steel and fiber containers.

Esso Research and Engineering Co. says tests on its RESIDfining process show that 90% desulfurization of many of the most readily available residuums is possible. This means refiners can meet legislative limits of 0.3–0.5% sulfur in fuel oil in many cases by direct desulfurization, Esso says.

American Hydrotherm Corp. has received a \$197,374 contract extension from the Office of Saline Water (osw) to operate a test and development facility at Wrightsville Beach, N.C. through August 1972. The company will provide information on design and performance of vertical tube evaporators.

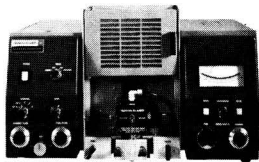
Envirotech Corp. has received a patent covering its Plural Purpose Furnace which combines lime reclamation and sewage sludge incineration. The device is said to eliminate the need for separate lime-reclaiming furnaces and disposal furnaces. Envirotech's incinerator uses sludge as fuel for process.

AMETEK has become exclusive worldwide licensee of Ventron Corp.'s proprietary sodium borohydride process for mercury removal. The process appears to be applicable to other heavy metals as well as mercury.

Beckman Instruments has supplied General Motors with seven complete emission measurement systems for end of assembly line testing of 1972 automobiles to be sold in California. The instruments monitor carbon monoxide, carbon dioxide, hydrocarbons, and nitric oxide on a continuous, automatic basis.

Determine pollutant metals with our Model 103 Atomic Absorption Spectrophotometer.

AA spectrophotometry is increasingly used to determine metallic elements in waters, effluents, brines, impinged air samples, and other materials that can be dissolved or suspended.



Our new Model 103 is easy to use and priced so low many laboratories can fully equip themselves for under \$4,000. Yet, it includes many features formerly available only on very expensive instruments—if at all.

The 103 reads directly in concentration of the element. The zero-concentration reading is set by touching an auto-zero button. It includes integration, which improves precision while speeding up analyses. (You can determine one element in one sample in about ten seconds.)

For details, write for our 16-page bulletin "Techniques and Applications of Atomic Absorption." Instrument Division, Perkin-Elmer Corporation, 771 Main Avenue, Norwalk, Connecticut 06852.

PERKIN-ELMER

Circle No. 15 on Readers' Service Card

Experience, equipment, technology and help are available for problems on:

- oil-water separations
- water clarification
- waste-water treatment
- sedimentation
- water re-use, recycle
- lime slurry systems

Please send details of your problem to expedite evaluation and reply.

**ENVIRONMENTAL PRODUCTS DEPARTMENT,
DENVER EQUIPMENT DIVISION, Joy Manufacturing Company**

600 Broadway, Box 5268, Denver, Colorado 80217

Telephone (Area Code 303) 244-4466

Offices and plants throughout the world

**DENVER
EQUIPMENT
DIVISION**



Circle No. 25 on Readers' Service Card

Systems Research Laboratories, a Dayton, Ohio R&D firm, will purchase a controlling interest in **Systems Technology Corp.**, also of Dayton. Systems technology is an environmental and pollution control company.

North American Rockwell's Science Center has received a \$1.7 million contract from California's Air Resources Board for a major air chemistry study in three of the state's air basins. Several university and state agency scientists will collaborate with NR.

Westinghouse Electric Corp. has signed an agreement with the Lybian Arab Republic to build a \$15 million power generation and water desalination plant in Zuara, Lybia. The unit will provide 3 million gpd of potable water.

Zurn Industries, Inc., has acquired Wilkins Regulator Co. (Los Angeles, Calif.) for an undisclosed amount of cash and notes. Wilkins manufactures automatic pressure-reducing valves.

Combustion Engineering has been given a \$13.5 million contract by Illinois Power Co. for a 600-MW controlled circulation coal-fired steam generator.

Quemetco, Inc. (City of Industry, Calif.) has ordered six more modular air filtration units from Wheelabrator-Frye, Inc. (Mishawaka, Ind.) for use on two non-ferrous recycling plants.

The American Petroleum Institute has awarded a \$152,201 contract to Ocean Design Engineering Corp. (Long Beach, Calif.) for testing of a device for recovery of oil-soaked adsorbents from oil spills. The company will test its Aquamarine Model H-650, originally designed as a weed harvester, to see if it can recover oil-laden straw and foamed polymers.

Esso Research and Engineering Co., has been awarded a \$200,000 one-year contract by the Coordinating Research Council (CRC) and the Environmental Protection Agency (EPA) for a continuing study on the sources of polynuclear aromatics (PNA) in auto exhaust and the fate of these compounds in emission control systems.

BUY an ADVANCE® Chlorinator ...GET a Company

When you buy an ADVANCE Model 201 gas chlorinator for water and wastes treatment you get more than just the finest instrument of its kind. Behind every Model 201 chlorinator is an organization devoted solely to chlorination, providing you with engineering "know-how," experience, and a one year unconditional equipment guarantee... When needed, ADVANCE offers fast 24 hour "turn-around" factory service, unmatched in the industry.

All this adds up to ADVANCE RELIABILITY, so essential to the maintenance of health and sanitation. Write for Bulletin 916.

CAPITAL CONTROLS CO.
ADVANCE LANE, COLMAR, PA.,
18915, U.S.A. 215-822-2901



Circle No. 2 on Readers' Service Card

SEND US YOUR SAMPLES FOR ANALYSIS---



**SAVE TIME
AND MONEY.
RAPID SERVICE.
HIGH PRECISION.**

TRAPELO/West (formerly Tracerlab)

2030 WRIGHT AVENUE, RICHMOND, CALIF. 94804 Phone (415)235-2633
DIVISION OF LFE CORPORATION

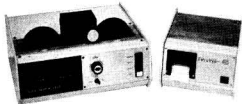


Circle No. 11 on Readers' Service Card

YOU CAN DEPEND ON US!



To provide the most advanced instruments for particles—sampling, generating, and monitoring.



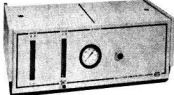
PAPER TAPE READER

Automatically evaluates sampler tapes in percent transmission or COH units; all solid-state circuitry with BCD output; features logarithmic converter to accommodate a wide range of sampling parameters for COH read-out; processes up to 480 spots per hour; meets ASTM standards; solid-state printer available.



TAG SAMPLER

Collects particles by impaction in nine stages; all stainless steel construction; permits isokinetic sampling of velocities from 500 to 2500 feet per minute by nozzle selection; retains particles by featuring low impaction velocity; temperature up to 1800°F; size ranges from 0.1 to 30 microns, plus in-line filter; ideal for stack and industrial application.



FLUID ATOMIZATION AEROSOL GENERATOR MODEL 7330

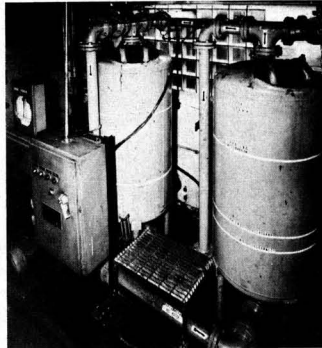
Size range 0.03 to 3 microns; output up to 1 billion particles per second; variable dilution rates; all stainless steel contact areas. electrically neutral aerosol; liquid or solid particles.

Call or write today for Instrument Catalog

ER ENVIRONMENTAL RESEARCH CORPORATION

3725 North Dunlap Street
St. Paul, Minnesota 55112 (612) 484-8591

You Can Depend on ERC



Filter media

New oil removal filter media holds 4-5 times as much oil as filter sand. Oil can be removed by water backflush. Removal efficiency is in 95% range. Hayward Filter Co. 61

Exhaust analyzer

GSM-300 Diagnostic Exhaust Analyzer measures carbon monoxide and hydrocarbon content and aids in diagnosis of engine troubles. Unit is double beam nondispersive infrared analyzer with Luft-type, gas-filled detector. GSM-300 features automatic gas calibration and is available in several ranges of pollutant concentration. Olson-Horiba, Inc. 62

Noise barrier

Portadamp is a magnetized, noise-reducing sheet material that can be applied directly to noise-producing mechanical equipment. Can reduce noise levels by as much as 25 dB. National Research Corp. 63

Calibrator

Model 8500 calibration gas source allows true dynamic accuracy in testing air quality analyzers. Instrument provides variable gas concentrations for accurate multipoint calibrations of linearity and response time. Monitor Labs, Inc. 64

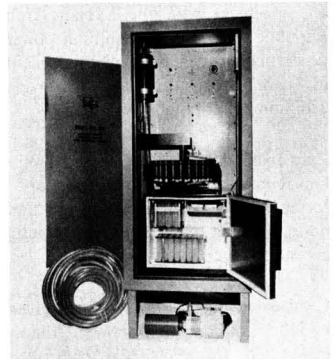
Odor incinerator

Simple, high-efficiency, straight stack fume incinerator can be used where there are no fume complications, and it is not desirable to recover heat. Units are

gas-fired, with 0.6 sec dwell time and maximum temperature of 1500°F. Midland-Ross Corp. 65

Sulfur analyzer

New sensor measures sulfur dioxide and sulfite in liquids without interference from color, turbidity, or salt concentration of solution. Threshold for SO₂ is 0.05 ppm. Probe membrane is impermeable for ions and large molecules. Sensor does not respond to other common dissolved gases. Ericsen Instruments 66



Liquid sampler

Electrically operated discrete/composite sampler can take either 24 individual 100-ml samples or a composite 1.5-gal sample. Standard unit is supplied with 1-, 2-, and 5-min sampling cams plus a 24 hr/7 day clock timer. ProTech, Inc. 67

Dredge

Portable, high-speed dredging scoop has a capacity from 3-50 yd³ and can dredge up to 1500 ft from shore. Unit is completely controlled from the shore and can be run by a single operator. Terra Marine Scoop Co. 68

Air sampler

Lightweight hi-vol sampler gives fast, accurate results without use of complicated sampling trains. Particulate matter is collected on a removable glass fiber filter. Standard equipment includes magnahelic gages, dial thermometer and control valves, plus a suction blower and flexible hose for sampling in difficult areas. Rader Pneumatics, Inc. 69

Circle No. 4 on Readers' Service Card

new products

Slurry system

Stor-Batcher System provides lime storage, automatic slurry makeup, and slurry feed for lime-using processes. Ratios of slurry components are readily variable, and the mix tank provides automatic keep-fill. Metering of slurry to process is controlled with a modulating valve activated via a pH sensor. Aerodyne Machinery Corp. 70

Bag filter

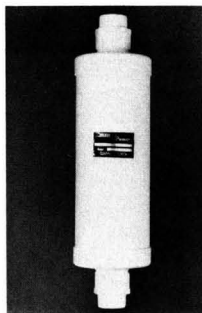
Oval bag Modu-Pulse Collector has been completely redesigned into separate modules to eliminate reentrainment of dust during pulse cycle. Tek-Air, Inc. 71

Oxygen bleaching

Specialized laboratory pressure reactor system for research on oxygen bleaching applications features stainless steel construction and precision-controlled heating rates. Units with pressure ratings of 150 psi or 300 psi available. M/K Systems, Inc. 72

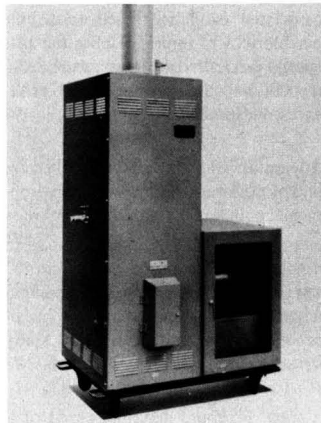
Conductivity-temperature meter

Hand-held, battery-operated Envirometer measures conductivity (50–2000 $\mu\text{mho/cm}$) and temperature (-10 – 40°C) in fresh water. Useful for determining dissolved solids. Beckman Instruments, Inc. 73



Muffler

Noise on air supply equipment can be reduced as much as 50% with noncorrosive air discharge muffler. Six models suitable for pressures up to 20 psi and temperatures up to 120°F are available. Engineered Products 74



Oil burner

Combination waste oil burner and water heater is designed to burn a wide range of used industrial or automotive lubricants. Burners have capacities ranging from 1.8–6.6 gph with heat recoveries ranging from 5000–35,000 Btu/hr. Barclay & Co. 75

Scrubber converter

Rod-conversion kit allows changing of any existing wet scrubber to venturi-type scrubber. Kit parts are installed inside the scrubber after internal parts are removed. Environing, Inc. 76

Cleaning ball

Pneumatic ball provides more efficient cleaning of sewer lines at lower cost. Elastomer ball is inflated until it fits the line and is floated through the sewer. Swirling water around ball pushes debris to manhole for easy removal. Cherne Industrial, Inc. 77

Dust filters

Preassembled dust filters are delivered factory-assembled ready for installation. Internal parts are already adjusted, saving as much as 35% on dust filter erection. W. W. Sly Manufacturing Co. 78

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

FREE

Wastewater Analysis Guide

HACH CHEMICAL COMPANY
P. O. Box 907
Ames, Iowa 50010 U.S.A.

HACH

Products for Wastewater Analysis

Hach Chemical has prepared a new, 16 page guide to assist municipal and industrial wastewater treatment plants in conducting the many water quality tests now required by pollution control authorities.

The guide lists each test, recommended methods and the chemicals, apparatus and glassware necessary.

For your free copy of the Hach Wastewater Analysis Guide, write:

HACH

Chemical Company

P.O. Box 907 • Ames, Iowa

50010 (515) 232-2533

"First in Water Analysis"

fresh insights on environmental issues



America's Land & Its Uses

Marion Clawson • This compact account of the nation's land and its many uses ranges from the three traditional uses of land—farming, grazing, and forestry—to the two that today pose the severest problems, urbanization and outdoor recreation. \$8.50, \$2.45 paper

Environmental Quality Analysis

Theory & Method in the Social Sciences
Allen V. Kneese & Blair T. Bower, editors • Today's environmental crisis calls for coordination among many disciplines—the sciences, economics, law, management, government. The authors offer a comprehensive approach for coping with the myriad problems of our beleaguered environment. \$12.00

Economics & the Environment A Materials Balance Approach

Allen V. Kneese, Robert U. Ayres & Ralph C. d'Arge • "It is as good reading for the amateur who wonders what the outcry of the environmentalists is all about as for the professional ecologist, residuals engineer, and economist."—*American Institute of Planners Journal* \$2.50 paper

Suburban Land Conversion in the United States

An Economic & Governmental Process
Marion Clawson • "Examines the complex relationships underlying land conversion in the United States."—*Public Works* \$12.50

Interbasin Transfers of Water Economic Issues & Impacts

Charles W. Howe & K. William Easter • "Provides a setting for consideration of large-scale transfers in terms of regional demands."—*Engineering Societies Library* \$9.50

Published for Resources for the Future, Inc.



**THE JOHNS HOPKINS
UNIVERSITY PRESS**
Baltimore, Maryland 21218

Circle No. 13 on Readers' Service Card

new literature

Perchlorate fumes. New 16-page publication reviews exhaust systems and associated equipment used to handle perchloric acid fumes. Publication lists special hazards, case histories, recommendations, and gives selected references. Plastic Fabricators, Inc. 91

Apparatus. Bulletin lists comprehensive line of glassware for analysis of environmental pollutants. Tudor Scientific Glass Co. 92

Spray irrigation. Technical bulletin describes use of Aquatower to dispose of process wastes and sewage by spray irrigation. McDowell Mfg. Co. 93

Alarms. Brochure describes seven of a series of environmental hazard monitors for sensing visibility, wind, precipitation, atmospheric electricity, etc. Kahl Scientific Instrument Corp. 94

Osmosis systems. Revision of general brochure on osmosis systems gives greater emphasis to reverse osmosis and details operating costs. Contains graphs showing pressure-temperature effects. Osmonics, Inc. 95

Filters. New line of Pall Guard filter housings and cartridges is designed to protect pneumatic systems from sludge, oil, water, and dirt over widely varying flow rates. Bulletins detail sizing information and operating specs. Pall Trinity Micro Corp. 96

Water treatment. Bulletin covers all types of mechanical aeration for waste treatment and describes line of mixers and aerators. Flow charts give typical designs and applications. Mixing Equipment Co. 97

Water system evaluation. Fifty-page publication appraises some 38 basic features of a water supply system to aid a utility manager in determining if systems are up to snuff. Johns-Manville 98

Mercury kit. Data sheet describes new mercury detection kit which uses a colorimetric reaction to determine mercury concentrations as low as 100 ppb. Koslow Scientific Co. 99

Flow recorder. Bulletin describes Gravity Flo-Recorder unit which provides accurate volume flow record. Operating specs and typical applications are given. BIF SaniTrol, Inc. 100

Analytical service. Literature describes BGI/Werby Hi-Vol filter analysis service. Billings & Gussman, Inc. 101

Cooling water contaminants. Reprint of article on controlling contaminants in cooling water discusses types of microbial contamination and their control, and gives information on corrosion inhibitors, antifoulants, and treatment costs. Drew Process Chemicals 102

Water testing. Data sheet lists recommended equipment and supplies available keyed by number to Water Pollution Control Federation standard tests and company catalog. Fisher Scientific Co. 103

Temperature recorder. Literature describes operating specifications and uses of Model 3070 Film Recording Thermograph, suitable for continuous unattended monitoring of air or water temperatures. General Oceanics, Inc. 104

Waste burner. Publication describes use of Populated Area Combustor for burning gaseous refining or chemical processing wastes with maximum community acceptance. National Airoil Burner Co. 105

Marine toilet. Illustrated 12-page brochure outlines advantages of an evaporative toilet system which eliminates discharge of sewage by vessels. Unit is suitable for installation in fixed remote areas. General American Transportation Corp. 106

Particle monitor. Bulletin describes fully automatic stack particulate monitor that continuously measures and records emissions with an accuracy of ± 0.002 grains/ft³. Research Appliance Co. 107

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

Disposal of Sewage and Other Waterborne Wastes. Karl Imhoff, W. J. Muller, D.K.E. Thistlethwayte. 2nd rev. ed. x + 305 pages. Ann Arbor Science Publishers, Inc., Drawer No. 1425, Ann Arbor, Mich. 48106. 1971. \$16.80, hard cover.

Standard reference work covering, in detail, the problems of liquid waste disposal including industrial effluents and water pollution control. Source of information for all engineers, chemists, and medical officers as well as sewage and public health authorities and water conservancy boards. ■

Dimensions of Change. Don Fabun. ix + 230 pages. Glencoe Press, 8701 Wilshire Blvd., Beverly Hills, Calif. 90211. 1971. \$8.95, hard cover.

Illustrated in full color, this six-part publication deals with technological responses to behavioral change that may

take place in the next 30 years. Sections are titled: Ecology, Shelter, Energy, Food, Mobility, and Telecommunications. ■

This Endangered Planet: Prospects and Proposals for Human Survival. Richard A. Falk. 495 pages. Random House, Inc., 201 E. 80th St., New York, N.Y. 10022. 1971. \$8.95, hard cover.

Analysis of four factors (war system, overpopulation, depletion of natural resources, and deterioration of the environment) underlying the ecological crisis that now endangers the earth, according to the publishers. ■

Manual of Wastewater Operations. C. H. Billings, D. F. Smallhorst, Eds. xiv + 755 pages. Texas State Dept. of Health, Austin, Tex. 78700. 1971. \$10.00, hard cover.

This fourth edition, with every chapter updated, attempts to serve better those

interested in the art and science of waste water collection and treatment. Could be described as operators writing a manual for their profession. ■

Matheson Gas Data Book. William Braker and Allen L. Mossman. xviii + 574 pages. Matheson Gas Products, P.O. Box 85, E. Rutherford, N.J. 07073. 1971. \$17.50, hard cover.

Provides information for more than 130 different gases. Discusses toxicity, handling and storage, leak detection, and disposal, to name a few areas. ■

The Outlook for Water: Quality, Quantity, and National Growth. Nathaniel Wollman, Gilbert W. Bonem. xxviii + 286 pages. Johns Hopkins Press, Baltimore, Md. 21218. 1971. \$12, hard cover.

The authors construct an economic model for a national water perspective based on regional analyses. By com-

(Continued on p 180)

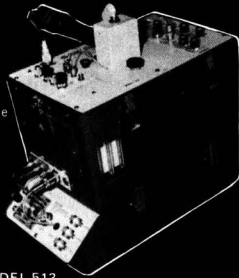
PORTABLE SULFUR ANALYSIS

Features

Battery or Line Operated
Completely self contained gas supply
Oven and Detector individually heated
Teflon sampling system available
Teflon Column

Applications

Determine Low Level Sulfur Compounds
Optional Total Sulfur/GC Operation
Stack Gas Analysis
Source Surveying



MODEL 513

The performance proven concept (over 2½ years in operation) of portable gas chromatography has now been extended to include the analysis of Sulfur compounds. The Flame Photometric Detector is available on the Model 513 and gives the specificity and sensitivity which is desired for this type of analysis. Built in gases and batteries make this instrument completely independent of all external supplies for a minimum of 8 hours.



ANALYTICAL INSTRUMENT DEVELOPMENT, INC.
250 So. Franklin Street, West Chester, Pa. 19380
Tel: (215) 692-4575

Circle No. 23 on Readers' Service Card

Type any technical symbol into your reports.

Typit can supply you with any symbol you want. We have over 1200 now in stock, and can make additional symbols to meet your requirements. Typit symbols are used world-wide by industry, education, and government.

These symbols easily adapt to your present typewriter (even a Selectric). For further information write for free catalog or call: Typit Division, Mechanical Enterprises, Inc., 5249 Duke Street, Alexandria, Virginia 22304.

Phone: (703) 751-3030



MECHANICAL ENTERPRISES



Circle No. 28 on Readers' Service Card



SOLID WASTES

A new publication of the American Chemical Society puts the nation's solid waste problems in perspective.

A 96-page book entitled "SOLID WASTES" contains 26 articles that first appeared in *Environmental Science & Technology*.

Among the topics covered are:

- Incineration
- Pyrolysis of plastics
- Electricity from waste
- Federal government programs
- Fly ash utilization
- Auto hulk disposal

and many others

The book can only be obtained from the Society and is not available in any bookstore. It costs just \$2.00.

Order from:

Special Issues Sales - E
American Chemical Society
1155 16th St., N. W.
Washington, D. C. 20036

paring the impact of alternative quality goals on policy, Dr. Wollman and Mr. Bonem explain how aesthetic judgments can be incorporated into an economic analysis of water resources. ■

Manual for Activated Sludge Sewage Treatment. Brian L. Goodman. v + 197 pages. Technomic Publishing Co., Inc., 265 W. State St., Westport, Conn. 06880. 1971. \$15, paper.

Manual was printed in 1966 as "Notes on Activated Sludge" and intended as lecture notes for technical meetings. The requests for copies became so numerous that this is the third printing of the manual which has been rewritten and sections added for updating. ■

Highways and Our Environment. John Robinson. xii + 340 pages. McGraw-Hill Book Co., 330 W. 42nd St., New York, N.Y. 10036. 1971. \$24.50, hard cover.

Illustrated book provides a focal point against which citizens and groups can act more intelligently and more forcefully than they have in the past, concerning the environment and the increased number of highways. Traces the history of roads in the world. ■

Water Pollution, Disposal, and Reuse, Vols 1 and 2. J. E. Zajic. xii + 389 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, N.Y. 10016. 1971. \$22.75 and \$16.50, respectively, hard covers.

Written for anyone interested in water and its purification, these books were specifically designed as interdisciplinary textbooks for a water pollution engineering course at the University of Western Ontario. Intended for every environmentalist—student, scientist, and engineer. ■

Ground Water: A Selected Bibliography. Frits van der Leeden, Ed. viii + 116 pages. Water Information Center, Water Research Bldg., Manhasset Isle, Port Washington, N.Y. 10050. 1971. \$15, hard cover.

Approximately 1500 references listed under 32 topics, each dealing with a particular aspect of the field of groundwater hydrology. ■

Automotive Emission Control. William H. Crouse. vii + 136 pages. McGraw-Hill Book Co., 330 W. 42nd St., New York, N.Y. 10036. 1971. \$3.50, paper.

Designed to be an authentic source of information for everyone interested in

atmospheric pollution and its control. The interested layman will find the answers to his questions on automotive pollution and what he can do and have done to his car to alleviate the problem. ■

Water Resource Law and Policy in the Soviet Union. Irving K. Fox, Ed. viii + 256 pages. University of Wisconsin Press, Box 1379, Madison, Wis. 53701. 1971. \$8.50, hard cover.

The Soviet Union and the U.S. share similar problems and situations, among which both have encountered major conflicts among water users and uses and the effect on environmental quality of water programs in an industrial society. Since the two nations attack these similar problems with widely differing systems, this book explains Soviet water resources management. ■

Prevention and Control of Oil Spills. 552 pages. American Petroleum Institute, c/o Publication Management Corp., 898 National Press Bldg., Washington, D.C. 20004. 1971. \$12.50, hard cover.

Simultaneously published with the Conference on Prevention and Control of Oil Spills and reviews the state-of-the-art of oil spill prevention, control, and cleanup. This reference work contains all papers presented at the conference as well as 21 additional papers. ■

Environment Index. 600 pages. Environment Information Center, Inc., 124 E. 39th St., New York, N.Y. 10016. 1971. \$50 (regularly \$75), hard cover.

Multiple entry index to the key literature of 1971. Lists 42,000 entries representing coverage from scientific, technical trade, and general magazines, government reports, conference papers and proceedings, newspapers, books, and films. Also listed are environmental control patents, major legislation introduced, and names and addresses of state and federal pollution control officers. ■

Games

Litterbug. Urban Systems Engr. Co., 1033 Mass. Ave., Cambridge, Mass. 02100. 1971. \$5.00.

Game for children 4 to 10 years old emphasizes ecology. Players move trash barrels about the board via colored cubes and collect trash as they move through the community, therefore stopping the "litterbug." ■

meeting guide

February 20-23

American Institute of Chemical Engineers

AICHE 71st National Meeting
Dallas, Tex.

Many sessions on various phases of pollution control. Contact: R. S. Schechter, Dept. of Chem. Eng., Univ. of Texas, Austin, Tex. 78712

February 21-22

Environmental Protection Agency and Clemson University

Coastal Zone Pollution Management Symposium
Charleston, S.C.

Focuses attention of regional, state, and local agencies on water quality problems in the coastal zone. Write: Billy L. Edge, Co-Director, Coastal Zone Pollution Management, Rhodes Engineering Research Center, Clemson Univ., Clemson, S.C. 29631

February 23-24

EPA, Washington State Dept. of Ecology, and NOAA

Symposium on Oil Pollution, the Environment, and Puget Sound
Seattle, Wash.

Provides current information regarding oil pollution problems in Puget Sound and the Pacific Northwest and efforts to solve these problems. Write: Oil Pollution Symposium, P.O. Box 15320, Wedgewood Station, Seattle, Wash. 98115

February 24

Mogul Corp. and Engineering Society of Detroit

Water Pollution Seminar
Detroit, Mich.

Will give industrial firms a quick overview of all current legislation affecting water pollution control. Write: Engineering Society of Detroit, 100 Farnsworth, Detroit, Mich. 48200

February 25

St. Louis University School of Law and Underwater Research Institute

Environmental Communication Workshop
St. Louis, Mo.

Will bring together attorneys, scientists, and engineers to ensure effective use of environmental research in the American courts. Write: Environmental Communication Workshop, School of Law, St. Louis University, St. Louis, Mo. 63108

March 5-9

Society of Toxicology

1972 Annual Scientific Meeting
Williamsburg, Va.

For additional information, Robert A. Scala, Esso Research and Engineering Co., P.O. Box 45, Linden, N.J. 07036

March 11

Gannon College

Literature of the Environmental Crises Seminar
Erie, Pa.

Contact: Institute for Community Development, Gannon College, Erie, Pa. 16500

March 14-15

American Gas Association and others

GATE-SwRI Energy Conservation Forum
San Antonio, Tex.

Will consider conservation and ways of producing more energy. Write: Jack Wolfe, GATE Information Center, Southwest Research Institute, 8500 Culebra Rd., San Antonio, Tex. 78284

March 14-16

U.S. Bureau of Mines and IIT Research Institute

Third Mineral Waste Utilization Symposium
Chicago, Ill.

Registration accepted on an as-received basis. For details: Murray A. Schwartz, Symposium Chairman, IIT Research Institute, 10 W. 35 St., Chicago, Ill. 60616

March 16-20

National Association of Secondary Materials Industries

59th Annual Convention
Los Angeles, Calif.

Theme "National Leadership for the Recycling Industries." Contact: NASMI, 330 Madison Ave., New York, N.Y. 10017

March 20-24

Ohio State University

Midwest Workshop in Environmental Science
Columbus, Ohio

Contact: John Lindamood, Dept. of Food Science and Nutrition, Ohio State University, Columbus, Ohio 43210

March 21-23

Environmental Protection Agency and University of Houston

National Conference on Control of Hazardous Material Spills
Houston, Tex.

Write: H. Nugent Myrick, Associate Professor of Civil and Environmental Engineering, University of Houston, 3801 Cullen Blvd., Houston, Tex. 77004

March 26-28

Environmental Mutagen Society

1972 Meeting
Cherry Hill, N.J.

Write: Warren Nichols, Program Committee Chairman, Environmental Mutagen Society, Dept. of Cytogenetics, Institute for Medical Research, Copewood St., Camden, N.J. 08103

March 26-28

National Petroleum Refiners Assoc.

70th Annual Meeting
San Antonio, Tex.

Contact: National Petroleum Refiners Association, 1725 DeSales St., N.W., Suite 802, Washington, D.C. 20036

March 26-29

Environmental Division of American Institute of Chemical Engineers and American Society of Mechanical Engineers

Environmental Water Technology Conference
New Orleans, La.

Theme is "Process Wastewater Reuse in Industry." For more information: J. K. Rice, General Conference Chairman, Cyrus Wm. Rice Div., NUS Corp., 1910 Cochran Rd., Manor Oak Two, Pittsburgh, Pa. 15220

April 3-4

Oklahoma State University

Industrial Wastes and Advanced Water Conference
Stillwater, Okla.

Conference will bring together those responsible for producing wastes and those responsible for disposing of wastes to attempt to solve problems associated with both operations. Fee: \$12. Contact: Engineering and Industrial Extension, Oklahoma State University, Stillwater, Okla. 74074

April 5-7

International Association for Great Lakes Research

15th Conference on Great Lakes Research
Madison, Wis.

Contact: Gregory D. Hedden, Director, University Extension Sea Grant Program, 610 Langdon St., Madison, Wis. 53706

April 6-7

Research Triangle Universities and several national societies

National Symposium on Costs of Water Pollution Control
Raleigh, N.C.

Sessions include: Economic implications of national goals for water pollution control, economic incentives for pollution control, and economics of industrial waste management. Contact: F. E. McJunkin, Assoc. Director, Water Resources Research Institute, 124 Riddick Bldg., NCSU, Raleigh, N.C. 27607

(Continued on next page)

April 9-14

American Chemical Society

163rd ACS National Meeting
Boston, Mass.

For details: A. T. Winstead, ACS, 1155 Sixteenth St., N.W., Washington, D.C. 20036

April 10-12

North Carolina State University and others

Fourth Annual Air Pollution Workshop
Raleigh, N.C.

Program presents current and future goals concerning research on the effects of air pollution on vegetation and ways of communicating these goals between and among scientists and program planners at governmental levels. Contact: William A. Feder, Suburban Experiment Station, Univ. of Massachusetts—Waltham, 240 Beaver St., Waltham, Mass. 02154

April 18-19

Water Quality Research Council

1972 International Water Quality Symposium
Washington, D.C.

Symposium will explore the role of water quality in disease. Contact: David X. Manners Co., Inc., 237 E. Rocks Rd., Norwalk, Conn. 06851

April 20-21

International Association for Pollution Control

Annual Conference on Pollution Control and the Marine Industry
New Orleans, La.

Conference will cover legislation, regulations, standards, enforcement procedures, research and technology, and future concepts for environmental conservation. Contact: Carolyn Bloch, International Association for Pollution Control, Suite 700, 4733 Bethesda Ave., N.W., Washington, D.C. 20014

April 30-May 4

Institute of Environmental Sciences

18th Annual Meeting
New York, N.Y.

Sessions on curricula basics and implementation and reinforcement in environmental/ecological education and career guidelines for environmentalists. Write: Technical Program Committee, Institute of Environmental Sciences, 940 E. North-west Hwy., Mount Prospect, Ill. 60056

International

March 9-12

National Wildlife Federation

36th Annual Meeting and National Conservation Achievement Program
Mexico City, Mex.

Contact: T. L. Kimball, N.W.F., 1412 Sixteenth St., N.W., Washington, D.C. 20036

March 14

Institute of Physics

Acoustic Emission Conference
London, England

Contact: Meeting Officer, Institute of Physics, 47 Belgrave Sq., London SW1X 8QX

April 11-13

University College and International Association on Water Pollution Research

Phosphorus in Fresh Water and the Marine Environment Conference
London, England

K. J. Ives, Dept. of Civil & Municipal Engineering, University College London, Gower St., London W.C.1., England

May 15-17

Clean Air Society of Australia and New Zealand and the University of Melbourne

Clean Air Conference
Melbourne, Australia

Write: The Organizing Secretary, 1972 Clean Air Conference, National Science Centre, 191 Royal Parade, Parkville, Victoria 3052, Australia

June 5-16

United Nations

United Nations Conference on the Human Environment
Stockholm, Sweden

Attendance officially limited to government delegations. Extra seats on a first come, first served basis. Write: Whitman Bassow, Senior Public Affairs Officer, United Nations Conference on the Human Environment, Rm. 1061J, United Nations, New York, N.Y. 10017

June 18-24

International Association on Water Pollution Research

6th Annual International Conference on Water Pollution Research
Jerusalem, Israel

For information: Israel Host Committee, P.O.B. 16271, Tel-Aviv, Israel

November 3-9

Sewage Engineering Association of the German Federal Republic and others

International Sewage and Refuse Engineering Exhibition and European Sewage and Refuse Symposium
Munich, Germany

Address inquiries to: Wissenschaftlicher Leiter des EAS 72 Munchen, Gunter Muller-Neuhaus, Technische Universität Munchen, D-8000 Munchen 2, Arcisstrasse 21, West Germany

July 1973

AAAS and National Council of Science and Technology of Mexico

1973 Inter-American Scientific Meeting
Mexico City, Mexico

Includes air and water pollution discussions. Contact: American Association for the Advancement of Science, 1515 Massachusetts Ave., N.W., Washington, D.C. 20005

Call for papers

April 1 deadline

American Water Resources Association

Eighth American Water Resources Conference
St. Louis, Mo.

Papers invited in the following areas: water quality considerations (surface water and groundwater); water supply interactions; modeling interactions, social, legal, and economic interactions; and data techniques. Contact: D. L. Warner, Technical Program Chairman, Geological Engineering Dept., University of Missouri—Rolla, Rolla, Mo. 65401

Courses

February 22-24

American Water Works Association

Emergency Planning Short Course
San Mateo, Calif.

Designed to enable water utility managers to plan for disasters and minimize damage and continue utility operations. Contact: Director of Education, AWWA, 2 Park Avenue, New York, N.Y. 10016

March 4, 11, and 14

California State College

Statistical and Probability Analysis of Hydrologic Systems Short Course
Los Angeles, Calif.

Designed for engineers, hydrologists, and geophysicists. Contact: Office of Community Services, California State College, 5151 State College Drive, Los Angeles, Calif. 90032

March 6-7

USDA Graduate School

Policy Issue Seminar on the Quality of the Environment
Washington, D.C.

Will discuss environmental degradation and why it occurs or can occur in the future. Nominations due before Feb. 21. Fee: \$95. Write: Dee W. Henderson, Suite 265, National Press Bldg., 529 14th St., N.W., Washington, D.C. 20004

March 7-9

University of California Extension

San Francisco Bay-Delta Water Quality Short Course
Berkeley, Calif.

Fee: \$125. Focuses on research, regulations, waste management practices, and control policies for water quality enhancement. Contact: Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

professional consulting services directory

REYNOLDS, SMITH AND HILLS
ENGINEERING DIVISION

and affiliate




environmental engineering, inc.

Offer diversified services in Pollution Abatement, Resource Management and Environmental Consultation.

Problem Evaluation • Research and Development • Planning • Reports • Design • Supervision • Program Management

HOME OFFICE
Box 4850, Jacksonville, Florida 32201



DAMES & MOORE


Consulting Engineers in Applied Earth and Life Sciences

Air Pollution, Water Pollution
Solid and Liquid Waste Disposal
Environmental Studies for Nuclear Power Plants

Two Pennsylvania Plaza, New York, New York 10001

With Offices in Principal Cities Throughout the World

Kem-Tech Laboratories, Inc.



AIR AND WATER POLLUTION CONSULTANTS
ENVIRONMENTAL STUDIES • INDUSTRIAL PLANT INVESTIGATIONS • MOBILE LABORATORY SURVEYS • PRE-PLANT STUDIES

16550 Highland Rd. Baton Rouge, La. 70808



BRANDT ASSOCIATES, INC.
RD #1 Blue Hen Industrial Park
Newark, Delaware 19711
Phone (302) 731-1550

COMPLETE WATER ANALYSIS SERVICE
COMPUTERIZED ATOMIC ABSORPTION
HEAVY METALS
FLAMELESS MERCURY TO 0.2 PPB
BOD-COD-TOC

CALIFORNIA TOXICOLOGY SERVICE, INC.

Analytical services for the industrial hygienist and environmental engineer. Airborne sampling services and special photographic studies available in SW area.

AIR BIOLOGICAL MATERIAL INDUSTRIAL WASTE WATER
trace metals-chemicals-drugs-solvents-gases

2333 W. THIRD ST.
LOS ANGELES, CA. 90057
(213) 387-7684

P&W Engineers, Inc.
ENVIRONMENTAL ENGINEERING CONSULTANT

309 W. Jackson Blvd., Chicago, Ill. 60606 • 312 427-2700

Building and Facility Design
Air and Water Pollution Control
Waste Disposal Systems
Materials Handling Systems
Municipal Engineering Services

GENERAL TESTING LABORATORIES, INC.

Chemical and Biological Testing for Pollution Control

Lead, Mercury and other Metals by Atomic Absorption

Water and Air Analyses — since 1930 —

1517 Walnut Street
Kansas City, Mo. 64108
Phone — 816-471-1205


ECOLOTRON, INC.

1211 Stewart Ave., Bethpage, N.Y. 11714
(516) 938-6622

Wastewater Analysis Noise Surveys
Pilot Plant Studies Equipment Leasing
Treatability Studies Design & Consulting

THE BEN HOLT CO.
521 E. Green Street, Pasadena, Calif. 91101

ENVIRONMENTAL
• IMPACT STATEMENTS •
• ENGINEERING •



Stewart Laboratories, Inc.
820 Tulip Avenue • Knoxville, Tennessee 37921
615-525-5811

• Complete Water Quality Analytical Services
• Pre-operational Environmental Studies • Stream Pollution Surveys

Specialists in Trace Metals Analysis including Mercury and other Heavy Metals

ENVIRONMENTAL POLLUTION CONTROL SERVICES



Galson
Technical Services, Inc.
Environmental Sciences Division

6601 Kirkville Road, East Syracuse, N.Y. 13057
Tel: (315) 437-7181

Laboratory and Process Development

Industrial Waste Water Control

Liquid and Solid Incineration

Air Pollution Control

In-plant Control and Process Modifications

Desalination

CATALYTIC, INC.
Consultants • Engineers • Constructors
Environmental Systems Division
1528 Walnut Street, Philadelphia, Pa. 19102
215-KI 5-7500

CHARLES R VELZY ASSOCIATES, INC.
CONSULTING ENGINEERS

WATER POLLUTION CONTROL • SOLID WASTE DISPOSAL • AIR POLLUTION CONTROL • INDUSTRIAL WASTES • DRAINAGE • WATER SUPPLY

350 Executive Boulevard
Elmsford, New York 10523
Mineola, New York Babylon, New York



RYCKMAN/EDGERLEY/TOMLINSON and ASSOCIATES
Consulting Engineers Specializing in Water Solids and Air Pollution Control

12161 Lackland Road, St. Louis, Mo. 63141
Phone: (314) 434-6860

Washington, D.C. • Memphis, Tenn. • Dayton, Ohio
Chicago, Illinois • Bryan, Texas • Casper, Wyoming
Northumberland, England

ENPROX™
SERVICE AND CHEMICAL SYSTEMS

industrial water treatment pollution control

ENVIRONMENTAL PRODUCTS DIVISION OF working with industrial water 62 years

OAKITE

OAKITE PRODUCTS, INC.
BERKELEY HEIGHTS, N.J. 07922 • TLX 138661

professional consulting services directory

Complete capabilities in environmental monitoring

Laboratory Analysis, Consultation and Field Surveys

Third Party monitoring for Industry, Government Agencies, Institutions and Individuals

Call collect: 505 982-9841

Controls for Environmental Pollution, Inc.
1925 Rosina St., Santa Fe, New Mexico 87501

WOODWARD-ENVICON, INC.
Environmental Consultants

AIR • WATER • SITE PLANNING • WASTE • NOISE
A SYSTEMATIC MULTI-DISCIPLINE APPROACH TO ENVIRONMENTAL IMPACT REPORTS AND FIELD SURVEYS

1373 BROAD STREET, CLIFTON, NEW JERSEY 07012

Clifton, N.J. 201 473-6044 San Diego, Calif. 714 225-9381 Atlanta, Ga. 404 255-9541 New York, N.Y. 212 695-6766

A Subsidiary of Woodward-Clyde Consultants

SpectroChem
LABORATORIES INC.

545 Commerce St. 901-337-4774
Franklin Lakes, N. J. 07417

- Atomic Absorption
- Chemical
- Optical Emission
- X-ray Spectrometry

Analytical Services for the Environmental Engineer & Industry

CROBAUGH LABORATORIES
SINCE 1894

AIR AND WATER POLLUTION
Sampling — Measurements
Analysis — Consulting

COMPLETE LABORATORY SERVICE
Chemistry—Metallurgy—Spectroscopy
Particle Size Analysis—Atomic Absorption
Infrared—Chromatography—X-Ray Diffraction

216-881-7320
3800 Perkins Ave.
Cleveland, Ohio 44114

NORTH AMERICAN WEATHER CONSULTANTS
ROBERT D. ELLIOTT, EINAR L. HOVIND
Certified Consulting Meteorologists

- POLLUTION CLIMATOLOGY
- INSTRUMENTATION
- METEOROLOGICAL EVALUATION

Santa Barbara Municipal Airport,
Goleta, California 93017
Phone: 805-987-1246

FREEMAN LABORATORIES, INC.
Chicago Specialists

AIR & WATER POLLUTION SERVICES

- Complete stack and ambient air surveys
- Monitoring instrumentation systems
- Trace metal analyses, including Mercury
- Characterization of particulates and powders
- Water cooling techniques
- Consultation

8290 Evenhouse Ave., Rosemont, Ill. 312/696-3300

WATER ANALYSIS
Metals — Pesticides — T.O.C. — Etc.
Government approved procedures.
Phone or write for further information.
GALBRAITH LABORATORIES, Inc., Box 4187
Knoxville, Tenn. 37821, (615) 548-1335

richard terry environmental & assoc.  **environmental science & services**

116 N. CAROUSEL ST. ANAHEIM, CAL. 92806


- ENVIRONMENTAL IMPACT STUDIES
- SITE SELECTION
- SURVEYS

OVER 20 YRS EXPERIENCE Tel. 714/630 2930


Consulting Engineers

- Air & Water Pollution Control
- Environmental & Ecological Analyses
- Meteorological Studies
- Process Evaluation & Design
- Complete Laboratory Services

NUS CORPORATION
4 Research Place Rockville, Maryland
20850 (301) 948-7010

SIERRA 
RESEARCH CORPORATION


ENVIRONMENTAL SERVICES & SYSTEMS

- AMBIENT AIR MONITORING
- SITE SURVEYS
- METEOROLOGICAL ANALYSES
- COOLING TOWER EFFECTS
- AGENCY LIAISON AND EXPERT WITNESSES
- MONITORING AND DATA SYSTEMS

ENVIRONMENTAL SYSTEMS GROUP, P.O. BOX 3007
BOULDER, COLORADO 80303 • (303) 443-0384

THE C. W. NOFSINGER COMPANY
Pollution Abatement Through Experienced Process Planning Or Systematic Process Revamp

307 EAST 63 ST., P.O. 7239
KANSAS CITY, MO. 64113
PHONE: (816)-363-1460

 **THE CHESTER ENGINEERS**

- Waste Water Treatment • Sewerage
- Water Treatment • Supply
- Industrial Waste Treatment, Recovery and Reuse
- Air Pollution and Solid Wastes
- Landfills • Incineration
- Valuations • Rates • Management

Main Office: 845 Fourth Avenue, Coraopolis, Pa. 15108 • Kingston, Pa. 18704 (300 Market St.)

ENVIRONMENTAL ENGINEERS AND PLANNERS
DESIGN • RESEARCH • STUDIES

HEIL-POLLUTION SOLUTIONS

One source — one responsibility — that's HEIL for complete systems of pollution control — ventilating systems, corrosion-proof components, ducts and stacks, fume scrubbers, linings, coatings, plastic pipe.

WE DESIGN • BUILD • INSTALL
HEIL PROCESS EQUIPMENT CORPORATION
12909 Elmwood Avenue • Cleveland, Ohio 44111

TIDE STUDIES
ENVIRONMENTAL STUDIES & COASTAL HYDROGRAPHIC SURVEYS

TRI-COUNTY ENGINEERING, INC.

CIVIL & STRUCTURAL ENGINEERS
LAND PLANNERS & SURVEYORS
P.O. BOX 578 (813)-649-6241
NAPLES, FLORIDA 33941



USE THE CONSULTANTS' DIRECTORY

RATES PER MONTH

Size	6 months	12 months
1" x 1 col.	\$24.00	\$23.00
1" x 2 col.	48.00	43.00
1" x 3 col.	69.00	62.00
2" x 1 col.	48.00	43.00
2" x 2 col.	89.00	81.00

Your card may appear in every issue for one year, every issue for six months (consecutive issues), or every other issue for one year. Send your copy to

Joseph P. Stenza,
ENVIRONMENTAL SCIENCE & TECHNOLOGY
142 East Ave.,
Norwalk, Conn. 06851
or call him at 203-853-4488.

professional consulting services directory

TRC

ENVIRONMENTAL IMPACT REPORTS

APPLIED RESEARCH ENGINEERING CONSULTING

DIFFUSION METEOROLOGY STACK TESTING

ANALYTICAL LABORATORIES

The Research Corporation of New England
210 Washington Street Hartford, Connecticut 06106
(203) 527-4101

NOISE

Advanced Acoustical Research Corporation

1211 Stewart Ave., Bethpage, N.Y. 11714
(516) 938-6640

Specialists in Noise and Vibration Control

 **SCIENCE ASSOCIATES, INC.**

professional consultants on meteorological instrumentation to government, education, industry, and the public

Selection of the proper equipment depends on survey objectives, techniques of analysis, and funds available.

230 NASSAU STREET • BOX 230 N
PRINCETON, NEW JERSEY 08540
TELEPHONE: 609-924-4470

Ambient Systems Inc.

AIR Pollution • WATER Pollution • SEWAGE Treatment Consulting & Engineering

Equipment, Instrumentation, Systems Design, Specifications up to & including turn-key installations; surveys & sampling-airborne, ambient, industrial studies; maintenance & repair services.


P.O. Box 234 Hastings-on-Hudson, N.Y. 10706
(914) 693-5812

"Services to Public Works and to Industries with Emphasis on Environmental Compatibility"

M&E METCALF & EDDY ENGINEERS

Pollution Control Studies and Systems Design
Liquid Wastes • Solid Wastes • Air Pollution • Environmental Planning

Statler Building, Boston, Mass. 02116 • New York • Palo Alto • Chicago

 5901 OLSON MEMORIAL HIGHWAY
MINNEAPOLIS, MINNESOTA 55422

Environmental Systems
Gas Turbine Power Plants
Thermal and Superpressure Processes
Plant Activation • Plant Improvement
Gas Dynamics • Model Testing
STUDIES • DESIGN • TESTING

UNITED STATES TESTING COMPANY, INC.

1415 Park Avenue
Hoboken, N.J. 07030

ENVIRONMENTAL TESTING SPECIALISTS FOR:

AIR

- Stack and Source Sampling, Gases and Particulates
- Control Apparatus Efficiency Measurements
- Code Compliance, Evaluation, and Assistance

WATER

- Chemical and Biological Analysis
- Fish Toxicity Programs
- Management of Aquatic Environments
- Bioassay, Detergent Biodegradability

INDUSTRIAL

- Noise Surveys, Filter Testing
- Industrial Hygiene, Film Badge Dosimetry

Contact:
Environmental Sciences Division
John Pizzo
(201) 792-2400

erg TESTING LABORATORY

COMPLETELY COMPUTERIZED NEUTRON ACTIVATION ANALYSIS

Atomic Absorption
Mass Spectroscopy
Emission Spectroscopy
IR & UV Spectroscopy
Anodic Stripping Voltammetry
Gas Chromatography

Pesticides & Herbicides Biological Studies
Trace Element Studies
Environmental Sampling
Water Pollution
Air Pollution
in Plant & Stack Measurements

P.O. BOX 322
ANN ARBOR, MICHIGAN 48107
313-665-3477
ENVIRONMENTAL RESEARCH GROUP INC.

TERM INC.

Both long and short term pollution problems considered

terrestrial-land use studies performed

ecosystem modeling for digital and analog computers

resources studies designed, prepared and undertaken


management programs designed, computer-programmed and operated

ENVIRONMENTAL CONSULTANTS

Amos Eddy, Ph.D.
318 Royal Oak
Norman, Oklahoma
(405) 321-3375.

Joseph L. Goldman, Ph.D.
Houston, Texas
(713) 529-4891
Telex 762771

Julian Kinisky
Alberta, Canada
(403) 454-8757




Environmental Research & Engineering

Water and air pollution investigations. Thermal discharge studies. Ecological surveys. Instrumentation consulting.

 **LIMNETICS, INC.**

6132 West Fond du Lac Ave.
Milwaukee, Wis. 53218 • (414) 461-9500

 **INDUSTRIAL POLLUTION TESTING LABORATORIES, Inc.**

2907 Parnell Ave., Fort Wayne, Ind. 46805/Telephone 484-8723 (Area Code 219)

- Water & wastewater effluent evaluation by atomic absorption spectrophotometry, autoanalyzer systems & chemical analysis
- All analyses performed by college trained personnel
- Precision results at nominal fees
- Shipping containers furnished at no charge
- Discounting available for contractual agreements

Brochure & Fee Schedule available upon request

YORK RESEARCH CORP.

- Air & Water Pollution Control
- Complete Analytical Laboratory
- Source Testing & Stack Sampling
- Industrial Plant Investigations
- Noise Level Studies

Phone or write for our brochure

One Research Drive
Stamford, Connecticut 06904
(203) 325-1371

CLASSIFIED SECTION

IMPORTANT NOTICE

Various state laws against discrimination and the Federal Civil Rights Act of 1964 prohibit discrimination in employment because of sex unless based on a bona fide occupational qualification. Help wanted and situations wanted advertisements on these pages are for readers' convenience and are not to be construed as instruments leading to unlawful discrimination.

POSITIONS OPEN

ENVIRONMENTAL SPECIALISTS \$12,000-\$25,000

YOUR IDEAS ARE IMPORTANT... Does your present job satisfy your career objectives... Do you have experience in water pollution control, solid or liquid waste disposal, sewage plant and wastewater treatment design? Then you'll be interested in confidentially investigating the career opportunities now available. Send complete resume including present salary to S. Bondroff.

CROSS COUNTRY CONSULTANTS
Suite 300, 16 W. 25th St.
Baltimore, Md. 21218
Phone: 301/889-2894

All fees and employment costs paid by employer.

SALES APPLICATIONS ENGINEER

Position requires direct technical or sales experience with water quality agencies of government-Federal/State/Local-specifically related to pollution problems and instrumentation. Full responsibility for launching promotion and sales of automatic water quality monitors, market research and technical liaison, occasional travel. BS Physics (CE or EE) preferred. Salary commensurate with experience. Please submit resume to: Plessey Environmental Systems, P. O. Box 1447, San Diego, Ca. 92112

ENVIRONMENTAL ENGINEERS

We have many position openings throughout the U.S. for qualified professionals experienced in the design, application and/or sale of air, water, or waste pollution control equipment, chemicals and systems. Client companies pay fees. Send resume & salary history in confidence to Roger M. Hoffman.

ESSEX PLACEMENT ASSOCIATES
7 Central Square Lynn, Mass. 01901

GROWTH POSITIONS ENVIRONMENTAL SYSTEMS \$12,000-\$25,000

ENGINEERING-RESEARCH-MANUFACTURING MARKETING-MANUFACTURING APPLICATION

Fees company paid. Include present salary, minimum salary requirement and location flexibility with resume. Environmental Systems Div., Longberry Employment Service, Inc., 650 Niles Bank Bldg., Niles, Ohio 44446.

CLASSIFIED ADVERTISING RATES

Rate based on number of insertions used within 12 months from date of first insertion and not on the number of inches used. Space in classified advertising cannot be combined for frequency with ROP advertising. Classified advertising accepted in inch multiples only.

Unit	1-T	3-T	6-T	12-T	24-T
1 inch	\$48	\$46	\$45	\$44	\$42

(Check Classified Advertising Department for rates if advertisement is larger than 10".)

SHIPPING INSTRUCTIONS: Send all material to **Environmental Science & Technology, Classified Advertising Department, 142 East Ave., Norwalk, Conn. 06851**

INDEX TO ADVERTISERS IN THIS ISSUE

Advanced Acoustical Research Corporation	185	Plessey Environmental Systems	186
Ambient Systems, Inc.	185	REM, Incorporated	128
Analytical Instrument Development, Inc.	179	Milt Valera Advertising	
Mercer Associates		Research Appliance Company	108
Andersen 2000 Inc.	129	W. F. Mimick & Associates	
Brandt Associates, Inc.	183	Reynolds, Smith and Hills	183
W. R. Hollingsworth & Associates		Ryckman, Edgerley, Tomlinson & Associates, Inc.	183
Cajon Company	106	Science Associates, Inc.	185
Falls Advertising Company		Sierra Research Corp.	184
Calgon Corporation	104	B. P. Myer Associates, Inc.	184
Ketchum, MacLeod & Grove, Inc.	183	SpectroChem Laboratories, Inc.	184
California Toxicology Service, Inc.	175	Spraying Systems Company	134
Capitol Controls Company	175	Tri-State Advertising Company, Inc.	183
The Stuart Company		Stewart Laboratories, Inc.	183
Catalytic, Inc.	183	H. G. Swope & Associates	183
Arndt, Preston, Chapin, Lamb & Keen, Inc.		Technicon Corp.	IBC
The Chester Engineers	184	Mediad, Inc.	
W. S. Hill Co.		Teledyne Analytical Instruments	116
Climet Instruments	IBC	S. Michelson Advertising	
Bachrach Advertising		Term, Inc.	185
Controls for Environmental Pollution, Inc.	184	Richard Terry & Assoc.-Environmental Science & Services	184
Lewis E. Thompson Advertising		Trapelo/West	175
Crobaugh Laboratories	184	Cerrito Graphic Arts Advertising Agency	
Cross Country Consultants	186	TRC-The Research Corporation of New England	185
Nationwide Advertising Service, Inc.		Tri-County Engineering, Inc.	184
Dames & Moore	183	Union Carbide, Linde Div.	117
Denver Equipment Division, Joy Manufacturing Co.	174	Young & Rubicam, Inc.	
Frye-Sills, Inc.		United States Testing Company, Inc.	185
Dohrmann Div. Envirotech Corp.	101	J. R. Alison Company, Inc.	
Bonfield Associates		Charles R Velzy Associates, Inc.	183
Ecotrol Environmental Laboratory	183	Woodward-Environ, Inc.	184
Environmental Research Corporation	176	York Research Corp.	185
Jack Wenger Advertising, Inc.		Thomas A. Blanchard Associates	
Environmental Research Group Inc.	185		
Essex Placement Associates	186		
Fluidyne Engineering Corporation	185		
Freeman Laboratories, Inc.	184		
Galbraith Laboratories, Inc.	184		
Calson Technical Services, Inc.	183		
General Testing Laboratories, Inc.	183		
Hach Chemical Co.	177		
Wesley Day and Co., Inc.			
Heil Process Equipment Corporation	184		
Ashby Associates, Inc.			
The Ben Holt Company	183		
Howard, Needles, Tammen & Bergendoff	185		
Ind. Waste Treatment System—Fram Corp.	IFC		
L. P. Thompson, Inc. Advertising			
Industrial Pollution Testing Laboratories			
Johs Hopkins University Press	178		
Welch, Mirabile & Co., Inc.			
Joy Manufacturing Co., Denver Equipment Div.	174		
Frye-Sills, Inc.			
Kem-Tech Laboratories, Inc.	183		
Laboratory Equipment Corporation	106		
Imbs & Associates, Inc.			
Limnetics, Inc.	185		
The Brady Co.			
Linde Division, Union Carbide	117		
Young & Rubicam, Inc.			
Longberry Employment Service, Inc.	186		
Mechanical Enterprises, Inc.	179		
Holland-Coyte-Comberti			
Matheson Gas Products, a Division of Will Ross, Inc.	102		
Warner, Bicking & Fenwick, Inc.			
McGraw-Hill Book Company	134		
Metcalf & Eddy Engineers	185		
N. M. Salt Water Disposal Company, Inc.	134		
Pritchard Advertising			
The C. W. Nofsinger Company	184		
North American Weather Consultants	184		
NUS Corporation	184		
Compton Jones Associates, Inc.			
Oakite Products, Inc.	183		
Marsteller Inc.			
O'Brien & Gere Engineers, Inc.	185		
Olympus Corporation of America-Precision Instrument Div.	106		
Gallanos Advertising Agency, Inc.			
P & W Engineers, Inc.	183		
The Perkin-Elmer Corporation	174		
Gaynor & Ducas Advertising			
Advertising management for the American Chemical Society Publications			
CENTCOM, LTD. (formerly Century Communications Corp.) Edward P. Blanchard, President, Thomas N. J. Koerwer, Executive Vice President, 142 East Avenue, Norwalk, Connecticut 06851 (Area Code 203) 853-4488			
ADVERTISING SALES MANAGER Thomas N. J. Koerwer			
SALES REPRESENTATIVES Chicago 60601 . . . Gilbert C. Mueller, CENTCOM, LTD., 307 North Michigan Avenue, (Area Code 312) 641-0890 Dallas 75207 . . . Parker Harris, George Thompson, Roy McDonald Assoc., 714 Stemmons Tower West, (Area Code 214) 637-2444 Denver 80203 . . . Robert H. Heidersbach, Bud Foster, Roy McDonald Assoc., Inc., 846 Lincoln Street (Area Code 303) 825-3325 Houston 77006 . . . Frank N. Vickrey, Richard Clothier, Roy McDonald Assoc., Inc. 3130 Southwest Freeway, (Area Code 713) 529-6711 Los Angeles 90045 . . . Clay S. Holden, CENTCOM, LTD., Airport Arcade Bldg., 8820 S. Sepulveda Blvd., Suite 215, (Area Code 213) 776-0552 Norwalk 06851 . . . Anthony J. Giamanco, CENTCOM, LTD., 142 East Avenue, (Area Code 203) 853-4488 Great Britain and Western Europe . . . Brayton Nichols, The American Magazine Group, 27 Maddox Street, London, W. 1, England, Telephone—499-0180 Japan . . . Sumio Oka, International Media Representatives, Ltd., 1, Shibe-Kotohiracho, Minatoku, Tokyo			
PRODUCTION DIRECTOR Joseph P. Stenza			

ENVIRONMENTAL SCIENCE & TECHNOLOGY READER SERVICE

If you would like to receive any of the material made available by advertisers in this issue, circle the numbers on one of the attached cards corresponding to the number shown beneath each advertisement. The New Product and New Literature Digests also have corresponding numbers for each item. This is a free service provided by ES&T.

FEBRUARY 1972

VALID THROUGH
APRIL 30, 1972

ADVERTISED PRODUCTS:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
46	47	48	49	50	51	52	53	54	55	56	57	58	59	60

NEW PRODUCTS, NEW LITERATURE:

61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
106	107	108	109	110	111	112	113	114	115	116	117	118	119	120

Name _____

Position _____

Affiliation _____

Address _____

_____ Zip _____

NATURE OF BUSINESS Industrial Firm Academic Government
 Other _____

FIRST CLASS
Permit No. 25682
Philadelphia,
Pa. 19101

BUSINESS REPLY MAIL

No Postage Stamp Necessary if Mailed in the United States

POSTAGE WILL BE PAID BY—

**ENVIRONMENTAL
Science & Technology**

P. O. BOX 8639

PHILADELPHIA, PA. 19101



FEBRUARY 1972

VALID THROUGH
APRIL 30, 1972

ADVERTISED PRODUCTS:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
46	47	48	49	50	51	52	53	54	55	56	57	58	59	60

NEW PRODUCTS, NEW LITERATURE:

61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
106	107	108	109	110	111	112	113	114	115	116	117	118	119	120

Name _____

Position _____

Affiliation _____

Address _____

_____ Zip _____

NATURE OF BUSINESS Industrial Firm Academic Government
 Other _____

ENVIRONMENTAL SCIENCE & TECHNOLOGY READER SERVICE

FIRST CLASS
Permit No. 25682
Philadelphia,
Pa. 19101

BUSINESS REPLY MAIL

No Postage Stamp Necessary if Mailed in the United States

POSTAGE WILL BE PAID BY—

**ENVIRONMENTAL
Science & Technology**

P. O. BOX 8639
PHILADELPHIA, PA. 19101



If you would like to receive any of the material made available by advertisers in this issue, circle the numbers on one of the attached cards corresponding to the number shown beneath each advertisement. The New Product and New Literature Digests also have corresponding numbers for each item. This is a free service provided by ES&T.

FEBRUARY 1972

VALID THROUGH
APRIL 30, 1972

ADVERTISED PRODUCTS:

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45
46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

NEW PRODUCTS, NEW LITERATURE:

61 62 63 64 65 66 67 68 69 70 71 72 73 74 75
76 77 78 79 80 81 82 83 84 85 86 87 88 89 90
91 92 93 94 95 96 97 98 99 100 101 102 103 104 105
106 107 108 109 110 111 112 113 114 115 116 117 118 119 120

Name _____

Position _____

Affiliation _____

Address _____

Zip _____

NATURE OF BUSINESS Industrial Firm Academic Government
 Other _____

FIRST CLASS
Permit No. 25682
Philadelphia,
Pa. 19101

BUSINESS REPLY MAIL

No Postage Stamp Necessary if Mailed in the United States

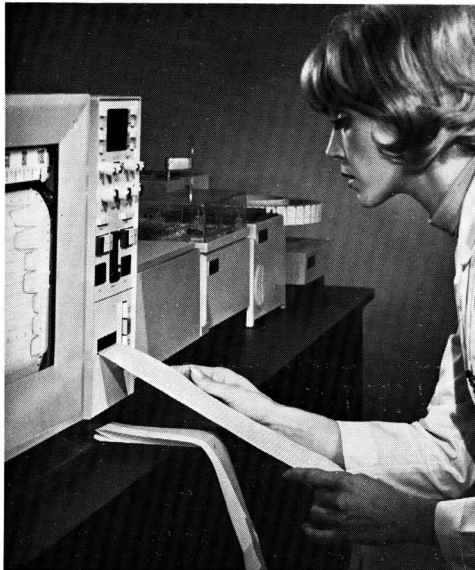
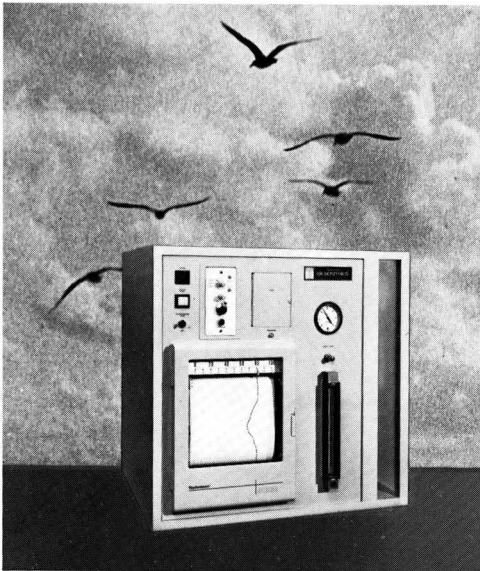
POSTAGE WILL BE PAID BY—

**ENVIRONMENTAL
Science & Technology**

P. O. BOX 8639
PHILADELPHIA, PA. 19101



There are two ways to analyze air quality.



Technicon does them both!

Air quality can be determined by continuous analysis of ambient air on-site, or by analyzing impinged samples in the laboratory. Technicon has AutoAnalyzer® systems that meet both these requirements.

The Air Monitor IV is a completely automated, compact, self-contained unit that is versatile enough to allow easy change of location and test parameters, and rugged enough to monitor many of the critical chemical constituents in air (including SO₂, NO₂, NO_x, total aldehydes (MBTH method), H₂S, F, NH₃, Cl₂, and total oxidants) 24 hours a day, every day.

For individual impinged samples, the Industrial AutoAnalyzer® II is the most advanced system for performing automated chemical analysis. It is capable of analyzing virtually any chemical constituent in air from impinged samples 10 times faster and at one-tenth the cost of manual methods. In addition, the unique design of AutoAnalyzer II analytical cartridges makes it easy to change

from one parameter to another in minutes.

Both the Air Monitor IV and AutoAnalyzer II utilize the principles of continuous flow analysis, which insure superior performance and results, sample after sample. Both systems use Technicon's new industrial colorimeter which permits linear readout of test results, with a telemetry output that facilitates data handling and storage capability.

An additional plus with all Technicon® systems is free training, unmatched service, and fast reagent order processing from any one of six distribution centers located throughout the United States.

For more information about Technicon AutoAnalyzer systems for air analysis, write to Department 131:



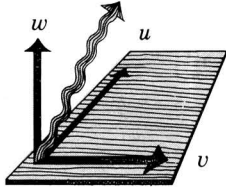
Technicon Industrial Systems

A Division of
Technicon Instruments Corporation
Tarrytown, New York 10591

How To Measure The Wind

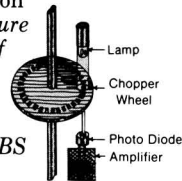
What is Wind?

For the purposes of air pollution measurement, wind is the movement of air in the biosphere relative to a fixed point on the surface of the earth. To describe the wind completely, it is necessary to measure three parameters (velocity, horizontal vector, vertical vector). In addition, for air pollution studies, it is often necessary to calculate "turbulence". *Climet Instruments is the world's leading manufacturer of accurate micro-meteorological instruments to record these wind parameters.*



Velocity

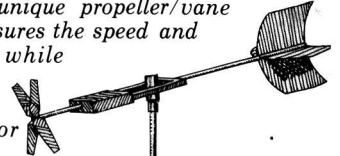
An accurate and reliable wind speed sensor is the anemometer. In order to build an anemometer responsive to very small wind changes, it is necessary to minimize internal friction and inertia. Climet's family of anemometers incorporates an optoelectronic pickoff to achieve low friction and inertia. *To assure accuracy, each set of Climet anemometer cups is individually balanced in a wind tunnel against an NBS calibrated anemometer.*



Climet's patented Ambiguous Point Logic System (APLS), virtually eliminates crossover discontinuities.

Vertical Vector

Air pollution research in such locations as "urban canyons" requires an accurate measurement of the vertical vector component of wind flow. *Climet's unique propeller/vane axiometer measures the speed and vertical vector while simultaneously recording the horizontal vector at the same point.* While it **directly** measures wind speed along the vertical vector, the axiometer's propeller-type wind speed sensor lacks the quick response of a cup-type anemometer. Where **indirect** vertical vector speed measurements are acceptable, Climet's Bivane is a more sensitive measurement system.



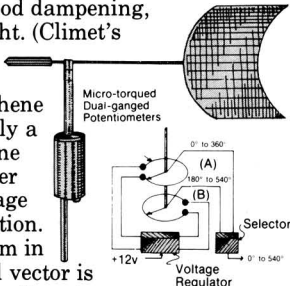
Turbulence

Turbulence (the rate and magnitude of the wind's variation about its primary direction of flow) is important as a cause of dispersion of polluted air masses. *Climet's unique Sigma Computer continuously calculates and records turbulence in analog terms along with real-time wind speed and direction data.* In addition to providing inexpensive on-site turbulence calculations, the Sigma Computer simplifies data collection and reduction as it records a **continuous** measurement rather than periodic samples.



Horizontal Vector

The horizontal vector (direction) of wind is universally measured by a wind vane. To insure fast response and good dampening, the vane must be light. (Climet's standard vane is molded in an airfoil shape from polyurethane foam and weighs only a few ounces.) The vane drives a potentiometer to produce a dc voltage proportional to direction. A significant problem in recording horizontal vector is the signal discontinuity at the potentiometer crossover point.



Details

Accurately measuring the wind is a complex task in which technological breakthroughs are rare...most of the real advances in wind instrumentation in the past five years have come from the micro-meteorological research team at Climet Instruments. Contact us for a free copy of *Meteorological Instrumentation in Air Pollution Studies*,...a detailed examination of the problems of air pollution measurement. *Climet Instruments, A Division of Wehr Corporation, 1240 Birchwood Drive, Sunnyvale, California 94086 Telephone (408) 736-6950.*

CLIMET