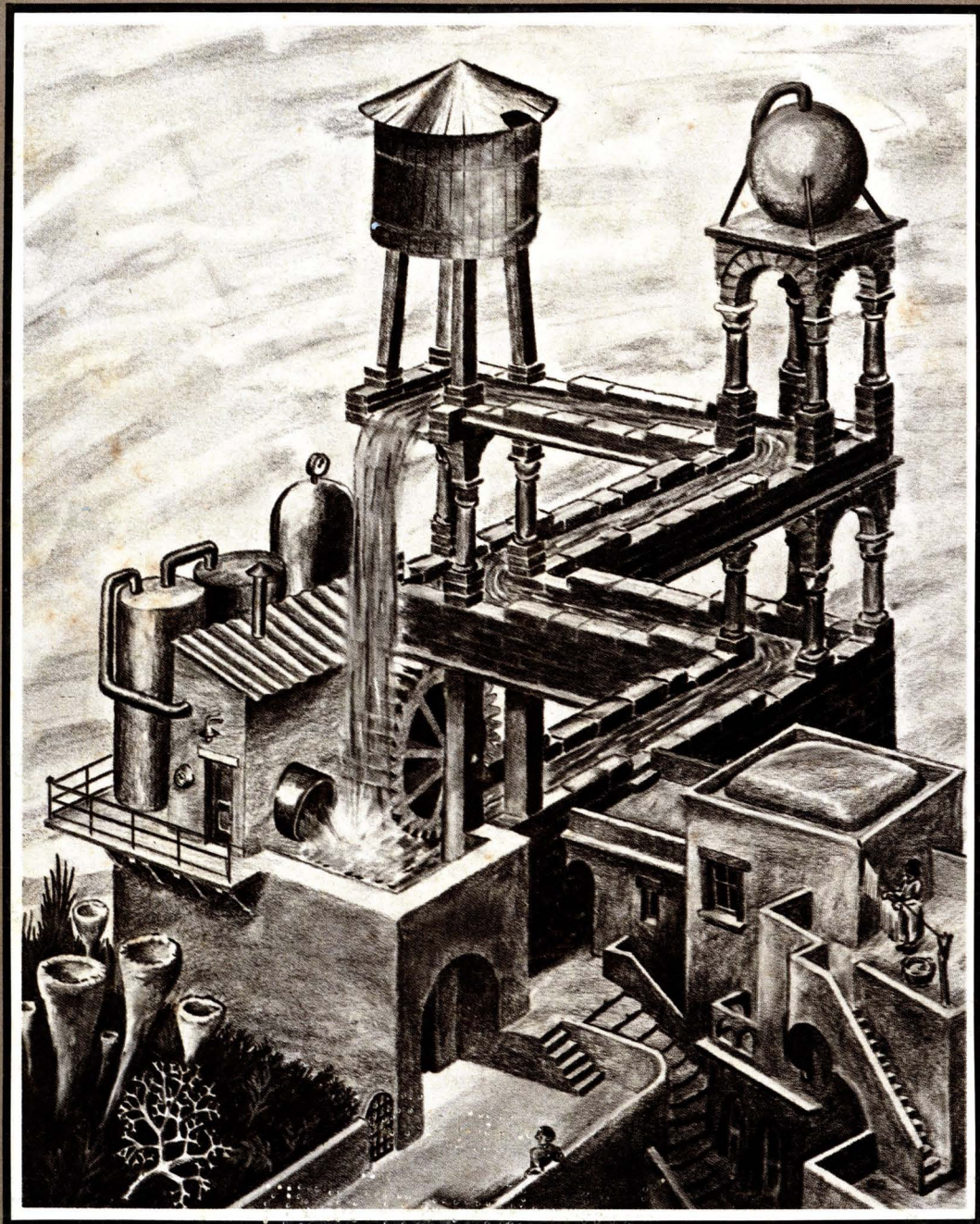


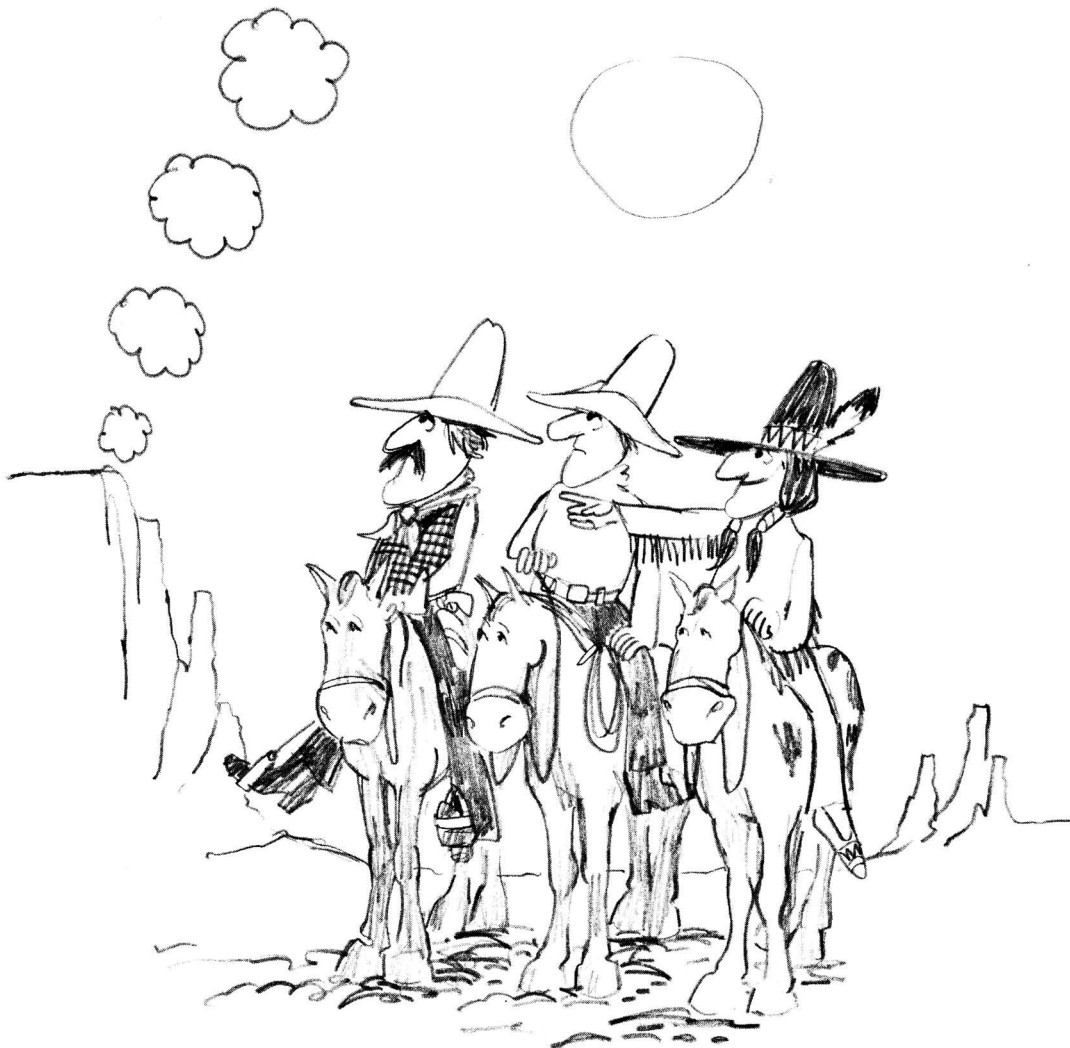
Environmental

Science & Technology

✓ OCTOBER 1974



Zeroing in on water pollution



Visual monitoring was fine for messages, but not for today's smoke regulations.

Smoke signals from an industrial stack just can't be deciphered by visual techniques anymore. Local, state and federal rules on particulate emissions necessitate continuous and far more accurate monitoring of smoke opacity.

To meet this need, Intertech is introducing the Model D-R 110 Optical Transmissometer. Mounted on-stack, the D-R 110 forms the heart of an automatic, unattended Emission Measuring System—a system that gives continuous, repeatable, highly accurate results. Output is linear with opacity or optical

recorder, an alarm, or to a control device on your process. Operation is virtually maintenance-free.

The Transmissometer works on the photoelectric dual-beam principle—where a light beam is transmitted across the stack, reflected back, and then “nulled” against a reference signal. The design and equipment have been widely used in Europe where stringent stack emission controls have long been in force.

In addition to the Transmissometer, the D-R 110 System includes mounting hardware, inlet filters, and where required, purge

air blowers, protective housings and chart recorders. Installation is simple and easy, but if you wish, we have the capability to handle it for you.

The Emission Monitoring System is one of many Intertech Systems that take the worry out of meeting air pollution regulations. For complete details, write or call Intertech, Dept. D.S., 19 Roszel Road, Princeton, New Jersey 08540. Phone: (609) 452-8600.

INTERTECH 
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CIRCLE 5 ON READER SERVICE CARD

CURRENT RESEARCH

- Quenching of singlet molecular oxygen by some atmospheric pollutants** 907
Ralf-Dieter Penzhorn,* Hans Güsten, Ulrich Schurath, and K. H. Becker

Deactivation of singlet molecular oxygen by several air pollutants was studied in a low-pressure reactor under static conditions. Emission at 7620 Å was taken as a relative measure of singlet oxygen in the system. The rate constants for deactivation by CH₃SH, dry air, and ambient air are compared with literature values.

- Photochemical reactivities of aldehyde-nitrogen oxide systems** 909
S. L. Kopczynski, A. P. Altshuler,* and F. D. Sutterfield

Photooxidation of formaldehyde, acetaldehyde, and propionaldehyde in the presence of NO_x produces the same products and biological effects as do hydrocarbon photooxidations. The reactivities of these aldehydes overlap those of the olefinic and aromatic hydrocarbons, and should be considered when formulating emission control strategies.

- Biodegradability of photodegraded polymers. I. Development of experimental procedures** 919
P. H. Jones, Durga Prasad, Michael Heskins, M. H. Morgan, and J. E. Guillet*

Biological oxidation of plastics in soils and sludge was studied using a modified Warburg apparatus. High-molecular-weight plastics resisted biodegradation, while degraded polyethylene and polypropylene showed significant oxidation rates.

- Biodegradability of photodegraded polymers. II. Tracer studies of biooxidation of Ecolyte PS polystyrene** 923
J. E. Guillet,* T. W. Regulski, and T. B. McAneney

Oxidation of a polystyrene-vinyl ketone copolymer in soil and sludge was followed using a radiotracer technique. The photodegraded copolymer was more biodegradable than the undegraded polymer. Biodegradation was slow, in keeping with the rates of biological degradation of natural products containing aromatic residues.

- Pressure drop and corrosion in zinc filters for mercury removal from waste streams** 925
P. Bro* and K. C. Lang

Zinc filter beds have high adsorptive capacity for removing mercuric ion from a simulated waste stream. However, accumulation of a zinc corrosion product led to high-pressure buildups, and dissolving the corrosion product caused high levels of zinc in the effluent.

* To whom correspondence should be addressed.

This issue contains no papers for which there is supplementary material in microform.

- Convenient method for generation of sulfuric acid aerosol** 930
R. L. Thomas, Venkatram Dharmarajan, and P. W. West*

A sulfuric acid aerosol is generated using an atomizer-burner mounted at the base of a miniature glass stack with a sampling probe at the top. A dilute H₂SO₄ solution is aspirated into the flame, producing water and SO₃. Recombination yields a sulfuric acid aerosol that can be used for evaluating analytical methods, or interlaboratory comparisons.

- Composition of organic constituents in breathable airborne particulate matter near a highway** 935
L. L. Ciaccio,* R. L. Rubino, and Jorge Flores

Particulates were collected along a New York City highway using Hi-Vol and Andersen samplers. Spectroscopic evidence shows the presence of aldehydes, ketones, acids, hydroxylic groups, possible oximes, organic nitrogen, and aza heterocyclic compounds arising from the combustion process in cars.

NOTES

- Adsorption of mercury from aqueous solutions by polyethylenimine-modified wool fibers** 943
G. N. Freeland, R. M. Hoskinson,* and R. J. Mayfield

Polyethylenimine-modified (PEI) wool had greater ability to adsorb mercury than unmodified wool. A capacity of 3.3 meq/g was achieved within 30 min with solutions of 1000 ppm. The mercury was easily desorbed, and the PEI wool used repeatedly.

- Removal of mercury from aqueous solutions by N-(2-aminoethyl)aminodeoxycellulose cotton** 944
S. L. Snyder and T. L. Vigo*

AEAC, formed by the reaction of ethylenediamine with chlorodeoxycellulose, was used for the adsorption of mercuric ion over a wide range of concentrations. The results suggest possible use of AEAC for collection of mercury in industrial processes.

Credits: 902, Graphics Unlimited (Belmont, Mass.)

Cover: Gerald M. Quinn (after a drawing, "The Waterfall," by M. C. Escher)

Calgon water report

Fall 1974

Niagara Falls Plant to Use Calgon Carbon

Calgon will supply 5 million pounds of Filtrasorb granular activated carbon and a \$330,000 custom-designed chemical feed system for the new 48-mgd physical/chemical sewage treatment system being constructed by the City of Niagara Falls, New York.

Scheduled for completion in 1976, the \$35-million plant will treat a highly complex mixture of industrial waste and domestic sewage prior to discharge into the Niagara River.

According to consultants Camp, Dresser & McKee, Inc., the physical/chemical treatment system will be one of the largest in the Country and the first of its kind in New York State. This type of system was selected for Niagara Falls because the wastewater contains refractory organics, such as color, and other organics toxic to biological processes.

Physical/Chemical Process

The physical/chemical process combines chemical clarification, using metal salts and polyelectrolytes for suspended solids removal, and adsorption with granular activated carbon, for removal of dissolved organics. Suspended solids, phosphates and COD will be reduced by 90,

(continued on page 4)

Research Underway On Toxic Chemicals Named by EPA

Toxic organic chemicals named in the Environmental Protection Agency's effluent standards, Section 307 (a) (2), Federal Water Pollution Control Act, can be removed from waste streams with granular activated carbon, according to Donald G. Hager, Director of Marketing for Calgon's Adsorption Systems group.

Hager made the statement upon com-

(continued on page 4)



The \$16-million expansion of Calgon's Big Sandy plant will be the fifth at this facility. Preliminary grading is now underway with startup scheduled for late 1975.

Calgon Begins \$31 Million Expansion of Carbon Facilities

New domestic and European construction programs will increase Calgon's granular activated carbon production capacity by over 50 million pounds per year.

Cost of the two projects is \$31 million, with completion scheduled for early 1976.

The expansion includes a completely new manufacturing plant in Feluy, Belgium, and the addition of another production line at its plant in Catlettsburg, Kentucky. The plant at Feluy and the new line at Catlettsburg will have approximately equal capacity, with the Belgian plant supplying the needs of Chemiviron, S.A., a Calgon subsidiary located in Brussels.

Capacity for Future

The new production facilities will provide adequate capacity for currently projected and long-term uses of granular carbon in a variety of markets and applications.

Calgon president Arthur L. Goeschel stated: "This production increase is a

major factor in the development of water management business, our single largest area of activity. Calgon carbons are in use in approximately 100 potable water treatment and water pollution control plants and in hundreds of food and chemical processing plants. Carbon also is being used in many industrial plants, and is under consideration by many others, for removal of toxic organic materials from plant effluents."

Promising Applications

Use of carbon for removing solvents and other organics from in-plant air and exhaust air streams is promising along with other applications such as control of odor at sewage treatment plants, Goeschel said. Also, more than 20 million automobiles use Calgon carbon to adsorb gasoline vapors that escape from fuel tanks and carburetors.

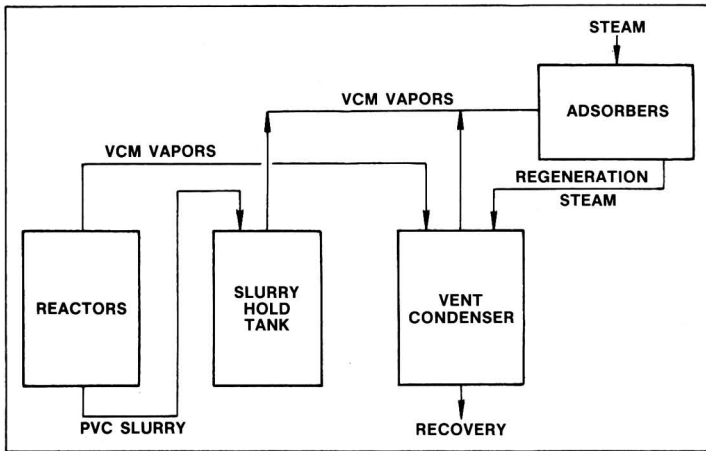
Calgon also operates granular carbon manufacturing plants at Pittsburgh, Pennsylvania, and Grays, Essex, England.

SPADNS Inaccuracy Linked to Sulphate Ion Carryover

Based on recent comparative studies of the fluoride ion electrode procedure and the currently approved SPADNS colorimetric procedure, Calgon analytical chemists R. F. Devine and G. L. Partington have recommended that the former be adopted as the approved procedure.

The SPADNS method was found to yield consistently higher fluoride readings than the electrode method. The chemists attributed this to carryover of sulfate ion in the distillation step.

The Devine/Partington report states: "All of the available methods for determination of fluoride in wastewaters require distillation to eliminate interferences and to assure recovery of all forms of fluoride. We have demonstrated, however, that sulfate ion carryover during distillation is considerable. Since sulfate ion causes a large positive error in the SPADNS colorimetric method, use of the method should be discontinued and the fluoride ion electrode procedure following distillation be adopted as the method of choice."



Simplified schematic of typical adsorption system arrangement for removal of VCM in PVC manufacturing plants.

Activated Carbon Effective For Removing VCM

Laboratory studies conducted at Calgon's research laboratories have demonstrated that granular activated carbon will readily adsorb vinyl chloride monomer (VCM) in concentrations ranging from 50 ppm to over 30% by volume. Using dual beds of activated carbon, 100% removal of VCM from both air and nitrogen streams has been shown to be technically possible in industrial applications.

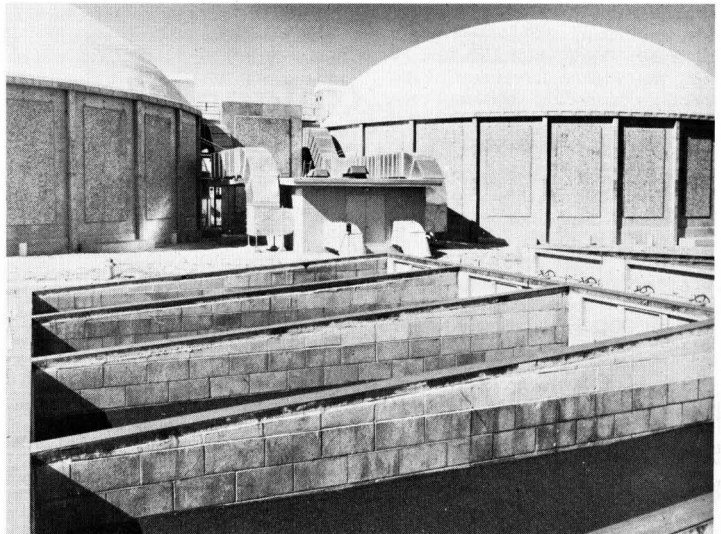
The study further demonstrated that VCM-saturated carbon can be regenerated in-place using either steam or hot nitrogen to desorb the VCM. By condensing VCM vapors in the regeneration stream, adsorbed vinyl chloride can be recovered and reused; allowing PVC and VCM manufacturers a return on their investment in the air pollution control system. Tests indicate that no polymerization occurs during regeneration.

A series of tests conducted to compare the VCM breakthrough capacities of various grades of activated carbon, under conditions of interest to VCM and PVC manufacturers, indicates that fine-pore, high-surface-area carbons such as Pittsburgh Type BPL and Type PCB are the most efficient; and that fine mesh size carbons produced longer break times.

On the basis of these breakthrough studies, it was concluded that activated carbon can remove essentially 100% of the VCM in air until breakthrough oc-

curs, at which time over 90% of the carbon bed is saturated with VCM.

A full-scale system is presently being installed by one manufacturer to recover vinyl chloride from its vent condensers and slurry holding tanks.



Sacramento Sewage Treatment Plant achieves zero odor through combined use of wet scrubbers and granular carbon adsorption. Located in a residential area, the Sacramento Main Waste Water Treatment Plant serves a population of 214,000 and 12 industries with an average flow of about 70 mgd and peak flows to 130 mgd. Following recent installation of secondary treatment facilities, odors drew heavy criticism from the community. Setting a goal of "zero odor," plant management decided to enclose the biological (trickling) filters (domed structures), pass filter emissions through sodium hypochlorite scrubbers to remove hydrogen sulfide, and then divert flow through 3-foot beds of granular activated carbon (foreground) to remove organic pollutants. Effectiveness of the initial installation has resulted in use of 300,000 pounds of Calgon® activated carbon throughout the plant to control all odors.

Another Calgon Bulk Blending Plant on Line

Calgon's third bulk chemical blending plant went on stream recently at City of Industry, California—near Los Angeles. Projected production includes a wide variety of water treatment products for Calgon's Boiler Chemicals, Cooling Water and Oilfield Chemicals departments.

The new facility enables Calgon's Water Management Division to provide overnight drum, rail car or tank truck delivery to customers throughout California, Nevada, Utah, Colorado and Arizona. Bulk liquid products are delivered directly to storage tanks at the user's plant. As part of the service, 350- to 8,000-gallon steel or fiberglass storage tanks are provided by Calgon.

Calgon also operates bulk chemical plants in Ellwood City, Pennsylvania and Bayport, Texas.

Fuel Oil Conditioner Stops Slagging and Plugging Problems for Paper Mill

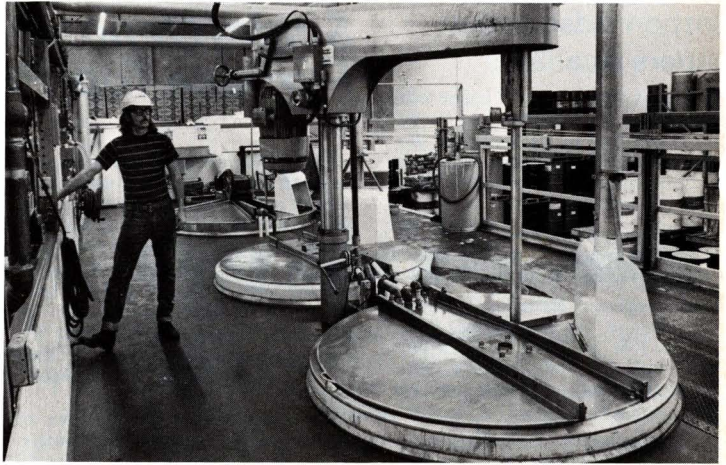
Between their 1970 startup and April 1973, recurring slagging on superheater tubes and severe plugging in a tubular air preheater caused considerable inconvenience, lost time and maintenance expense for a paper mill in the Northeast. Typically, 1,000 of the 4,000 tubes plugged after only 2-3 months of continuous operation.

Throughout the two-year period, several fuel oil additives were tried in an effort to eliminate the problems. All, however, proved to be either ineffective or too expensive.

During the Easter shutdown in 1973, a trial was started using Velvamag® Fuel Oil Conditioner. The single 600,000 lb/day power boiler consumes about 90,000 gallons of No. 6 oil per day, supplemented with barkwood. An optimum feed rate of one gallon Velvamag to 3,900 gallons of fuel oil was determined.

At the start of the trial, the superheater section was clean, but 500 tubes remained plugged in the air preheater. Three months later during the July shutdown, only a slight deposit existed in areas remote from soot blowers. This was washed away easily with water. During this shutdown, the air preheater was mechanically cleaned, leaving 50-100 tubes plugged. Velvamag treatment was continued.

Later, during the Labor Day shutdown, similar conditions were observed with not a single additional tube plugged other than those left plugged during the July cleaning. The conclusion was that



Two 1500-gallon and one 2000-gallon hydraulically-operated Cowles dissolvers are major components of the completely automated chemical production system at Calgon's new City of Industry bulk blending plant.

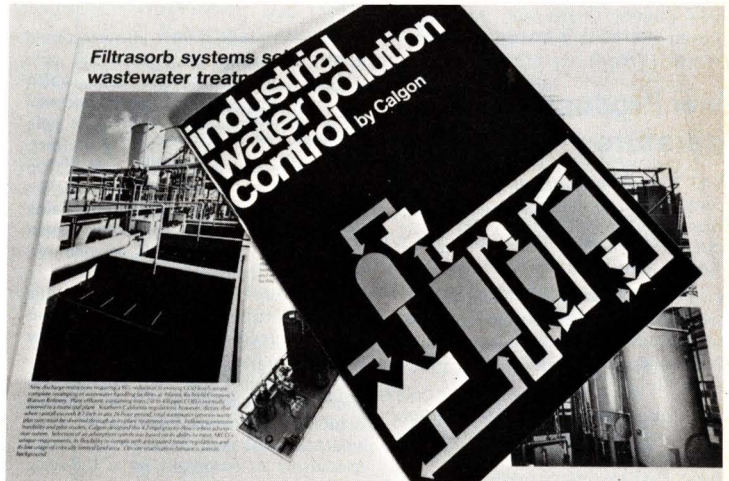
Velvamag had minimized problems that had existed for the previous two years.

Calgon fuel oil conditioners are now being used with similar success at two other mills operated by the same company.

Two new *Technical Information Reports*, (FC-101, FC-102) available from Calgon's Boiler Chemicals Department, discuss pre- and post-combustion problems associated with high-sulfur, high-vanadium fuel oils.

New Bulletin on Automated Feeders

Several variations of timed, metered-proportional and conductivity-controlled chemical feed and blowdown systems for boilers are described in this new bulletin. Also covered is a broad line of individual control units, feeding equipment and accessories that can be used to custom design systems to meet individual requirements. Request Bulletin No. B-5-086.



Industrial Water Pollution Control—a new 20-page, full-color brochure by Calgon—describes and illustrates through examples of operating client facilities Calgon's capabilities in industrial wastewater treatment.

Major topics include analytical and environmental services; granular carbon adsorption systems; polymers for water clarification; physical/chemical treatment; and the Calgon Adsorption Service for the control of toxic, refractory and other dissolved organics.

For a copy of *Industrial Water Pollution Control* by Calgon, request Bulletin 1-27.

Carbon Adsorption Papers Available

Copies of papers presented before technical societies are available at no charge. Address requests to Calgon Water Report, Public Relations Department, Calgon Corporation, P. O. Box 1346, Pittsburgh, Pa. 15230.

"Multi-Plant Applications of Carbon Adsorption Treatment," by E. N. Rebis, AIChE Meeting, Tulsa, March 1974.

"How to Cope with Hazardous Spills—A Case History," by W. Lawrence Ramsey and J. M. MacCrum, Joint AIChE/EPA National Conference on Hazardous Material Spills, San Francisco, August 1974.

"Use of Granular Activated Carbon for Industrial Wastewater Pretreatment," by R. H. Zanitsch and J. L. Rizzo, Ohio Water Pollution Control Federation, Toledo, June 1974.

"Removal of Toxic Organics from Wastewater by Adsorption with Granular Activated Carbon," by D. G. Hager and J. L. Rizzo, Technology Transfer Seminar, April 1974.

"The Use of Activated Carbon for Control of Paint Bake Oven Emissions," by J. E. Urbanic and W. D. Lovett, Air Pollution Control Association, Denver, June 1974.

"The Use of Activated Carbon for Controlling Odorous Air Pollutants," W. D. Lovett Conference, Pittsburgh, Lovett and R. L. Poltorak, Air Pollution March 1974.

New Product Literature

CL-63 Corrosion Inhibitor—liquid formulation of chromate and zinc ingredients used to control corrosion in recirculating cooling water systems—Bulletin No. 11-81.

BA-10 Antifoam—organic liquid formulation for control of foaming and solids carryover in steam boilers, even at high solids and alkalinity levels—Bulletin No. 10-78.

BA-11 Antifoam and Sludge Control Treatment—liquid formulation of polymeric sludge conditioner and anti-foam used to control solids carryover and accumulation of sludge and scale on boiler heat transfer surfaces—Bulletin No. 10-70.

LP-9 Boiler Sludge Control Treatment—liquid formulation of phosphate and polymeric conditioner used to prevent scale and sludge accumulation—Bulletin No. 10-72.

Scale/Deposit Inhibitor Solves Furnace Top-Pressure Problem

Closing the cooling water loop in a steel mill presents problems not encountered in once-through systems. At a mid-western mill operating two blast furnaces, the problem took the form of heavy scaling and deposit buildup in a Venturi scrubber on one furnace and the brick lattice countercurrent scrubber on the other. Keeping top pressure within tolerable limits required frequent acid cleaning and often resulted in unscheduled shutdowns.

During an unscheduled shutdown of the furnace equipped with the countercurrent scrubber, an analysis of the deposits revealed major constituents to be ferri-ferro cyanide and ferrous sulfite

with minors of calcium and magnesium. On the basis of this analysis and a visual inspection, it was decided to begin treating the countercurrent system with Calgon CL-14 Scale and Deposit Inhibitor.

One month later, the Venturi system had to be shut down for acid cleaning due to excessive top pressure. After being placed back on line, the Venturi system was also treated with CL-14. Acid cleaning had reduced top pressure from 200 to 190 psi. Afterward, however, top pressure continued to drop to about 175 psi. Monitoring of top pressure indicates that, besides preventing deposit buildup, the CL-14 is having a gradual cleaning effect on the system.

Since the CL-14 treatment program was initiated 10 months ago, neither furnace has had to be shut down for cleaning. Plant management has installed a 4,000-gallon storage tank and is now purchasing CL-14 by tank truck through Calgon Bulk Liquid Chemical Service.

Research Underway On Toxic Chemicals

(continued from page 1)

pletion of carbon adsorption studies conducted on endrin, aldrin, dieldrin, polychlorinated biphenyls, toxaphene, DDT, DDD and DDE. Benzidine was not included in the study because of its classifications as a carcinogen. Hager said benzidine appears to be adsorbable because of its molecular weight and chemical structure.

Concentrations of toxic chemicals used in the laboratory study were 100 ppb, with the exception of toxaphene, which was 500 ppb. Activated carbon reduced these concentrations to tenths of a ppb, well below proposed effluent guidelines. Toxaphene was reduced to 3 ppb. Extrapolation of test results indicates carbon required to treat wastewater containing these toxics at concentrations noted ranges from 3 to 58 pounds per one million gallons treated.

Laboratory tests also revealed that, due to their limited solubility in water, about 40% of the chemicals could possibly be removed by fine filtration.

Hager pointed out that although the laboratory test is reliable in determining feasibility of carbon adsorption treatment, it is not used to determine design parameters or economics on a full-scale system. This information is generally obtained by pilot testing under dynamic conditions.

"We consider the results of this preliminary study to be very encouraging," said Hager. "It is our intention to continue this research effort as other organic chemicals are added to the toxic chemical list."

Niagara Falls Plant To Use Calgon Carbon

(continued from page 1)

85, and 77 percent respectively. These reductions assure compliance with discharge regulations set by the New York Department of Environmental Conservation.

The completely automated chemical feed system will add polymeric coagulants and ferric-chloride to the waste prior to adsorption. Due to the large feed rates required, Calgon custom-designed a system that would make use of larger, but fewer, components. This allowed installation in a smaller area and considerably reduced capital cost, control problems and maintenance requirements.

28 Downflow Adsorbers

The adsorption portion of the system will consist of 28 downflow adsorbers, each containing approximately 165,000 pounds of Calgon's Filtrasorb® 300 granular activated carbon.

The carbon will be reactivated on site in a 6-hearth furnace with a daily capacity of 44,000 pounds. The furnace will be equipped with an afterburner and a scrubber to remove particulates from the exhaust.



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For author's guide and editorial policy, see

June 1974 issue, page 549, or write Katherine I.

Biggs, Manuscript Reviewing Office, *ES&T*

Talking about water cleanup

Discussion is good. It always has been and always will be. It's good on all matters—political and technical as well as social and personal matters. And so in Denver this month, the pros of the Water Pollution Control Federation meet at another annual conclave to discuss cleanup.

Everybody talks about it. In this issue *ES&T* talks all about water cleanup—the business, construction of best technology, and federal permit and monitoring requirements, as well as instrumentation, technical services, and analytical laboratories—and what many are doing about it.

In a special report, *ES&T*'s Josephson talks about the business of the wastewater treatment industry and how its more than 300 companies that make and sell products and services for cleanup in the municipal and private sectors view the future. Spokesmen from one of this nation's leading consulting engineering firms talk about the construction progress of the world's largest advanced wastewater treatment plant, when complete, in Washington, D.C., at Blue Plains.

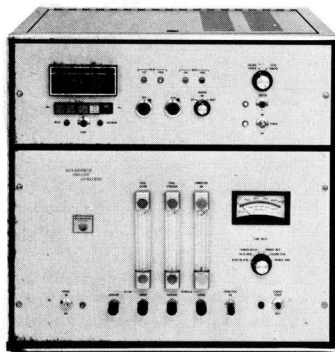
Federal spokesmen of the Environmental Protection Agency talk about the progress on permits and their monitoring requirements, while an industrial representative talks about water effluent monitoring instruments which give more reliable information in less time. Additionally, *ES&T* talks about a mobile testing van for checking new technological processes on old wastewater effluents, as well as a growing number of analytical laboratories that stand ready with both services and procedures for better analyses of water pollutants.

For the record, early last month EPA administrator Train met with President Ford to talk about water cleanup too, along with air cleanup, of course.

To those self-appointed critics who might refer to the old saying, "Everybody talks about it but no one does anything about it," we can only submit that talking about water cleanup must obviously come before any actual cleanup.



approved



total organic carbon
volatile organic carbon
total carbon

THE DOHRMANN® DC-50 ORGANIC ANALYZER makes all of these measurements accurately and rapidly. Based on proven, EPA approved* methods, it avoids interferences and undesirable pyrolysis reactions that historically have resulted in significant errors.

- **DIRECT READOUT:** Four-digit presentation shows carbon content directly in mg/liter or ppm. *No recorder needed!*
- **DIRECT MEASUREMENT:** A single sample injection gives either Organic Carbon or Total Carbon content *directly, not by difference.*
- **INDEPENDENT MEASUREMENT:** Volatile Organics are determined separately from Total Organics to aid in source identification.
- **RELIABLE MEASUREMENTS:** Determines important, lightweight volatiles such as low molecular weight alcohols and ketones, normally lost by acidification and sparging.
- **FAST:** 5 minutes per determination.
- **ACCURATE:** Repeatability of ± 1 mg/liter or $\pm 2\%$.
- **WIDE RANGE:** 1 to 2,000 mg/liter (ppm) without dilution.
- **PRICE:** \$7,875, including start-up assistance and operator training.

ENVIRONMENTAL PROTECTION AGENCY, WATER PROGRAMS, Guidelines Establishing Test Procedures for Analysis of Pollutants. FEDERAL REGISTER Vol. 38, No. 199, Part II, Oct. 16, 1973.

For brochures, reprints, or dates and locations of seminars, contact: DOHRMANN DIVISION, 3240 Scott Blvd., Santa Clara, CA 95050. (408) 249-6000. Telex 346 395.

ENVIROTECH



CIRCLE 16 ON READER SERVICE CARD

LETTERS

Reverse osmosis

Dear Sir: The feature authors (*ES&T*, July 1974, p 614) have presented a good picture of all of the pretreatment considerations necessary to install a reverse osmosis unit. They have further discussed the removal of various pollutants in general terms. The article could have been extremely valuable to engineers involved in pollution control if the data to which they allude had been quantified. Furthermore, the costs for these various pretreatment and reverse osmosis processes are as important and valuable as a judgment of the effectiveness.

David H. Furukawa
Fluid Sciences Division, UOP
San Diego, Calif. 92123

Radioactive slime ponds

Dear Sir: The report, "Reconnaissance Study of Radiochemical Pollution from Phosphate Rock Mining and Milling," details results of our investigation of the radiochemical pollution resulting from phosphate rock mining and milling. As you will note, the bulk of the report deals with problems resulting from milling. However, sufficient data exist to add to the article on slime ponds (*ES&T*, April 1974, p 312).

It has long been known that phosphate rock, especially Florida rock, contains uranium. What has not been widely recognized is that the rock also contains uranium decay products, one of the most hazardous of which is radium-226. Slimes tend to contain even more radium than the original ore. A common value, based on the literature and on our study, would be 45 picocuries per gram (pCi/g) of radium-226.

On this basis, the 1971 Cities Service slime-pond failure mentioned is calculated to have involved over 16.5 curies of radium-226. The total radium released to the environment from all slime pond spills is unknown but would probably add up to several hundred curies. One-and-one-half years after the Cities Service spill, the Peace River downstream of the spill contained over two times the USPHS Drinking Water Standard for

radium-226, as a result of leaching of radium from slimes deposited along the stream.

The article mentioned use of slimes for lightweight aggregate. The first decay product of the radium-226 contained in the slimes is radon-222, a radioactive gas which has received much notoriety as a result of the Grand Junction, Colo., use of uranium-mill tailings in home construction. The use of slimes in building construction must not be permitted.

The radiological problems of the phosphate industry do not end with the mining phase; in fact, they have just begun. The acidulation of phosphate rock to phosphoric acid results in a partitioning, during which the uranium remains with the fertilizer and most of the radium precipitates with the by-product gypsum. The gypsum solids contain approximately 25 pCi/g of Ra-226. A great deal of research effort is under way to develop methods to use by-product gypsum for wallboard. This is currently practiced in Germany. Such use unnecessarily exposes the population to hazardous levels of radon decay products, as was the case in Grand Junction.

An acid solution, known in the industry as "contaminated water" is used for transport of the gypsum solids. This material contains 90-100 pCi/l. of radium-226, which is 30 times the maximum permissible concentration (MPC) for radium, and three times the AEC standard for unrestricted areas. General industry practice is to recycle this water, with no discharge except during periods of high precipitation. However, some mills located along the lower Mississippi River discharge contaminated water and/or gypsum solids directly to the Mississippi River.

The general industry practice is to place the acid (pH < 2) gypsum-pond decant in a pit, often a mined-out area directly in contact with a limestone aquifer. As a result, radium values as high as 79 pCi/l. have been detected in the shallow ground water around phosphate mills.

Jim V. Rouse
EPA National Field Investigations Center
Denver, Colo. 80225

CURRENTS

INTERNATIONAL

Oil spill prevention and cleanup, as well as effects of pollution on marine life, rare and endangered species monitoring, and sea life rehabilitation after major pollution incidents were among subjects of a U.S.-Soviet information exchange. This exchange was accompanied by a tour of the University of Rhode Island's Graduate School of Oceanography and EPA's National Marine Water Quality Laboratory, Narragansett, R.I., by four Soviet scientists. The exchange and tour are part of a program based on an agreement signed in 1972.

WASHINGTON

EPA deputy administrator John Quarles, Jr., announced that about 1500 employers in the Boston, Mass., area were subject to violation notices under that area's transportation control plan, if they did not submit parking reduction plans by August 19. Under the "Boston plan," to apply to 38 urban areas in the future, employers with 50 or more employees must submit mass transit and carpool incentive programs so that employee parking spaces may be reduced 25%. The Boston plan is designed to reduce carbon monoxide levels by 58% and hydrocarbon levels by 68% in order to protect public health, and save about 110 million gal/yr of gasoline if the plan is fully implemented.

EPA's guidelines for the thermal processing and land disposal of solid wastes were promulgated in final form in the *Federal Register* of August 14, 1974. These guidelines grew out of a development program which took many months. Copies of these guidelines in the *Federal Register* are available from Mr. Ed Cox, EPA, OSWMP, 5555 Ridge Ave., Cincinnati, Ohio 45268

The EPA's National Ecological Research Laboratory, Corvallis, Ore., is undertaking a 4-yr project to assess the environmental impact of a new coal-fired power plant on wildlife, vegetation, and soils. The region under study surrounds Colstrip, Mont., where five electric utility companies are jointly building two 330-

MW turbine generators, the first of which is to start up in June 1975. By 1979, four generators are to be supplying 2000 MW to the area. The study will cover observations of controlled ecosystem segments; changes, if any, attributable to pollution; and plant and animal life cycles.

Health, Education, and Welfare (HEW) Secretary Caspar Weinberger announced grants of over \$2.7 million so that civic groups and U.S. classrooms may focus on energy and environmental problems. Authority



HEW Secretary Weinberger

for these grants is given by the Environmental Education Act P.L. 91-516, under which a total of 109 projects in 37 states will be funded. This funding will also cover a 4-state cooperative effort on energy conservation leadership to be conducted in Colorado, Massachusetts, North Carolina, and Washington under Title V of the Elementary and Secondary Education Act. Teacher and teaching aid development will also be emphasized.

There is not enough water for announced energy development projects in the Rocky Mountains, according to the U.S. Department of Interior's Bureau of Land Management (BLM). BLM's unpublished report states that these energy (electricity, coal gasification, and oil shale) projects would eventually need 1,031,880 acre-ft/yr of water. This is 159,780 acre-ft more than can be made available each year, according to present water regulations which are part of the Colorado River compact and the 1944 treaty with Mexico. These agreements are to ensure that seven U.S. states and Mexico receive enough drinking and irrigation water from the Colorado River basin.

The Florida Current portion of the Gulf Stream embodies about 25,000 MW of kinetic energy, according to estimates of the National Oceanic and Atmospheric Administration (NOAA) of the Department of Commerce. NOAA says that about 2000 MW of this energy could be harnessed to generate electricity at a "competitive" price. Therefore, the agency recommended a research and development program to evolve a small working prototype of a system to harness this energy. If it works as hoped, such a system could bring about "clean" generation of electric power, especially for the heavily populated Florida east coast.

STATES

In New Jersey, Glenn Paulson, one of the nation's leading environmental scientists, has been appointed to the post of assistant commissioner for science in the Department of Environmental Protection (DEP). Paulson will handle the DEP's scientific assessment of problems such as energy or resource recovery from waste, Outer Continental Shelf oil exploration, deepwater ports, nuclear power plants, toxic materials, environmental contaminants, water fluoridation, and related matters. Previously, he was head of the Scientific Support Program of the National Resources Defense Council, Inc.

The City of Kaukauna, Wis., is meeting the state's 85% phosphorus removal requirement. Kaukauna, one of a few Wisconsin municipalities meeting this requirement, discharges its effluent into Lake Michigan. They are meeting the requirement consistently and successfully with the simple addition of chemicals, specifically, aluminum sulfate supplied by the Allied Chemical Corp.

Minnesota is the 15th state to assume control over the issuance of permits under the National Pollutant Discharge Elimination System (NPDES). By July 31, both the EPA and the Minnesota Pollution Control Agency (MPCA) had issued 395 permits including 153 municipal, 227 industrial, and 12 agricultural permits; by December 31, all of Minnesota's 1350 necessary permits must be is-

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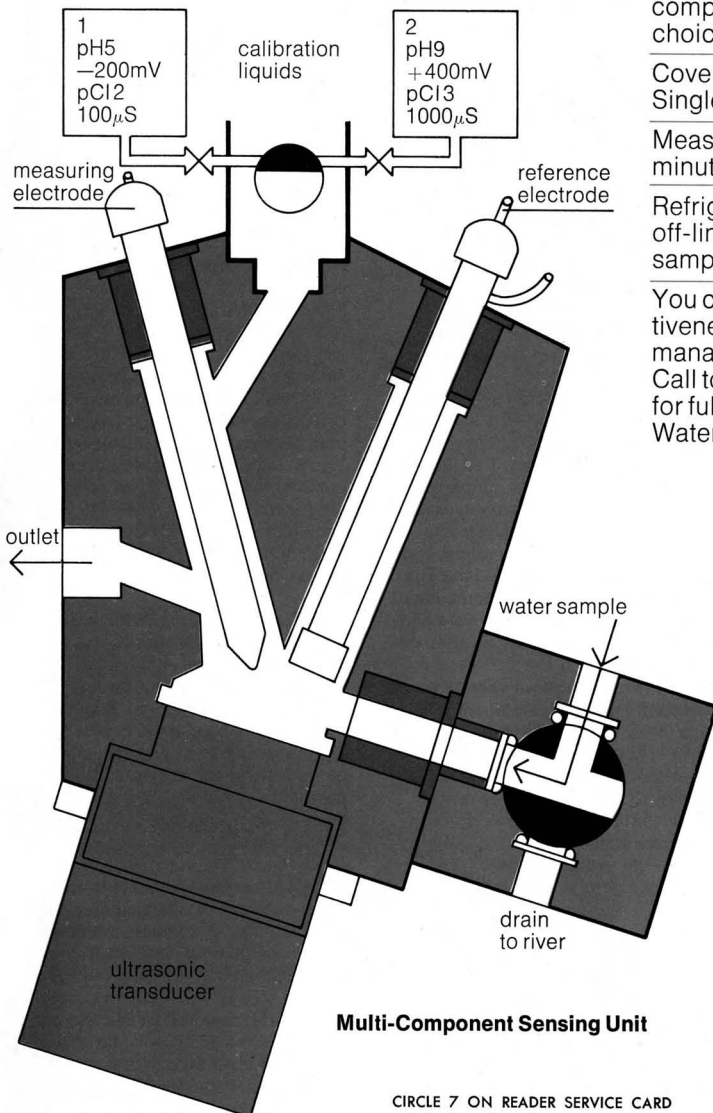
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Minnesota	Wisconsin

sued. The MPCA permits section is headed by Louis Breimhurst, and has its full staff of 22 employees.

The California Air Resources Board (ARB) has accredited Purzoust catalytic converters, made by Universal Oil Products Co. (UOP) for installation on pre-1973 cars. These converters are the first such devices accredited by the ARB. Tests of these converters on 100 cars gave results of 69% reduction in reactive hydrocarbon emission, 65% for carbon monoxide, and 14% for NO_x. UOP estimates that reactive hydrocarbon emissions, for example, could be reduced by over 100 tons/day in the Los Angeles area alone, if the 4.5 million cars and light trucks in the area were fitted with Purzoust systems.

California has created a State Energy Resources Conservation and Development Commission, which starts operations on January 7, 1975. The commission will preempt the Los Angeles County and other Air Pollution Control Districts' (APCD) authority to control, or grant or deny permits for new power plants. The new commission will have exclusive power to certify all sites and related facilities in California outside the permit area of the coastal zone. New power plants or plant additions of 50 MW or more capacity require certification; however, certification requirements will exempt new construction to begin up to January 7, 1978. Nevertheless, an APCD can take action if a violation of applicable air pollution laws does occur.

The Iowa Water Quality Commission (WQC) is proposing property tax exemption rules for installation of water pollution control devices. These property tax exemption rules are allowable because of a law passed by the 1974 Iowa legislature which sets

forth certain property tax exemptions for the installation of water pollution control devices in the state.

The Maine Department of Environmental Protection (MDEP) is making technical assistance teams available to inspect disposal sites for septic sludge and solid waste. Teams each consist of two engineers, an engineering technician, and a geologist. They will assist municipalities in complying with Maine's solid waste management regulations which require provisions for public sites for solid waste disposal. Teams would inspect such sites to determine whether the site can be economically converted to meet MDEP standards. If so, the team will advise the municipality on suitable changes; if not, the team will advise the municipality on economical site shutdown.

The Colorado Department of Health (CDH) conducted a limited test for vinyl chloride. In 14 businesses in the metropolitan Denver area, it was found that 138 employees were working in areas with potential vinyl chloride exposure. It was also determined that only three of the companies were monitoring vinyl chloride in their air, and only 34 employees were being checked periodically. The CDH will try to locate other industries in Denver and elsewhere in Colorado, where vinyl chloride exposure potential exists, and then inspect with samplers and require corrective action.

MONITORING

The relative distribution of chemical constituents in solid pollutants can be measured by a microanalytical technique, according to Megruie Associates, Lexington, Mass. In situ measurements are performed on the relative abundances of nucleides within solid materials. Systems are designed to analyze gases released by laser volatilization from selected portions of a sample. The released gases are separated by standard techniques before detection by either mass spectrometry or counting. Sensitivities of less than 10⁻⁶ atom are readily attainable for many nucleides.

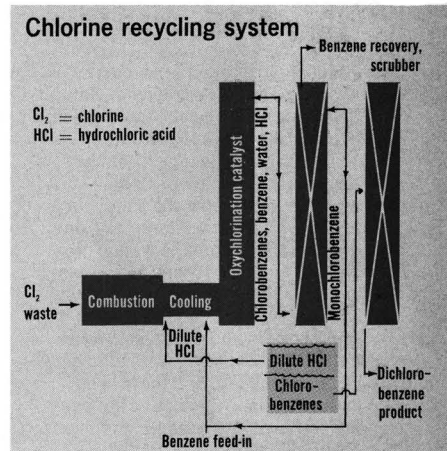
Automotive emission analysis will be done by computer-operated systems

to qualify cars for import to North America, as well as to countries within the European Community. The system consists of two test cells, each of which is operated by a process control computer, and four exhaust analyzer consoles. Each console measures the four important ingredients of exhaust gases. One person can control each test cell. The system was designed and built by Philco-Ford at Newport Beach, Calif., and is now in use at the Ford plant at Niehl, West Germany.

TECHNOLOGY

Total disposal of waste aboard ship is being practiced aboard the "Vistafjord," a one-year-old 25,000-ton cruise ship of the Norwegian America Line (NAL). All liquid waste is so intensively treated that only pure water is discharged overboard. The ship's garbage incinerator emits no smoke or fumes because of its special design. Bottles and cans are compacted and stored on board for proper disposal in port. This waste disposal system which, according to NAL, makes the "Vistafjord" "the most ecologically clean cruise ship afloat," was built into the ship with present, and possibly future pollution control rules envisioned by the ship's designers.

Recycling chlorine values from organic waste streams is possible because of a new process which uses oxychlorination to recover hydrogen chloride from such waste streams.



CURRENTS

The system can produce other salable products, such as mono- or dichlorobenzene. The process uses methods and equipment refined over 40 years in the Raschig oxychlorination process for phenol; thus, the process is immediately available. The process' inventor is Walter Prahl of Karlsruhe, West Germany, and licenses are available through Dynatron Research Corp., Madison, Wis.

Prevention of release of harmful organic fluids is achievable with a unique polymer developed for use in valves. The polymer will allow water to pass. According to what R. H. Hall and D. H. Haigh of Dow Chemical Co. told the American Institute of Chemical Engineers (AIChE), the alkylstyrene polymer will entrap organic liquids such as gasoline, hexane, benzene, and various chlorinated solvents. The polymer, in the form of beads, will swell in a valve-like device upon contact with these organic fluids, and seal off the release of these fluids.

Restoring polluted lakes by treating them with fly ash is a novel approach to fighting water pollution with air pollution. According to a team at the University of Notre Dame, fly ash is capable of freeing lake water of phosphates by "soaking them up." The fly ash also prevents phosphates on the lake floor from redissolving in the water when a 2-in.-thick layer of fly ash seals the lake bottom muds. The researchers say that the only major cost of the fly ash is its transport to the treatment site. A large-scale test will be made at Lake Charles East, near Angola, Ind. EPA is supporting this study.

Pollution abatement at no cost? Yes, according to the Academy of Natural Sciences, Philadelphia, Pa. Studies of the 512-acre Tinicum Marsh, which receives sewage treatment plant discharges, reveal that in summer, the marsh absorbs phosphorus at a rate of about 4.9 tons/day, and ammonia at 3.5 tons/day; and produces oxygen at 20 tons/day. Ruth Patrick, the curator of the Academy's limnology department, estimates that every stream and river can cleanse itself and eliminate wastes efficiently if not overloaded, or if there is no toxic material. The aquatic life does this work with no need for chemicals, electricity, or money.

INDUSTRY

The National Center for Resource Recovery (NCRR), Washington, D.C., is to act as technical adviser to the City of New Orleans to monitor the construction and operation of one of the first full-scale facilities in the U.S. for recovering reusable materials from municipal trash and garbage. The plant will process some 650 tons/day of refuse to reclaim glass, ferrous and nonferrous metals, and paper. Waste Management, Inc., Oak Brook, Ill., will construct the plant for the city.

Arthur Goeschel, president of Calgon Corp., said that protection of human health is the most important benefit to be realized from environmental control efforts. He believes that production and recreation benefits are "bonus" benefits which represent an



Calgon's Goeschel

extra payback beyond those which are to be realized in health, which Goeschel calls the most important area. Even though fully quantified data on health benefits are not available, "We cannot afford to delay action until a comprehensive evaluation can be made," Goeschel said.

The Metal Finishers' Foundation (MFF), Upper Montclair, N.J., has recently initiated a project aimed at removing heavy metals and cyanide from metal finishing effluent. The project is being conducted at Atomic International (AI) of Rockwell International Corp., Canoga Park, Calif., under the joint auspices of the MFF and the U.S. EPA. Scheduled over a 12-month period, the AI project focuses on a special process for cleaning up metal finishing plant effluents. The project involves a demonstration unit in support of which laboratory work is now under way.

Producers of construction materials can now use packaged dust control systems for quicker, easier compliance with air quality codes, according to the G. A. Kleissler Co., Edison, N.J. The company is offering complete dust control systems which include hoods, ducts, precleaners, cloth filter separators, and exhausters. Many systems can be laid out to fit needs ranging from floor tile of asbestos plants to transit mix cement plants and quarries. The company also runs surveys to identify a plant's dust generators, and recommends ways to meet air quality codes.

R. T. Willson, senior vice-president of the American Iron and Steel Institute, predicts that by 1980, household garbage used as fuel "will generate the equivalent of almost one billion gal of home heating oil or 5 million tons of coal annually." Willson points out that use of garbage for fuel is environmentally clean, and that the need for landfill sites would be all but eliminated. He also sees a related aspect of resource recovery in the reclamation of ferrous metal—mainly in the form of steel cans—from solid waste.

The American Petroleum Institute (API) has contracted with the Bermuda Biological Station for Research, Inc., for a field study on the effects of floating oil contaminants on plant and animal life found on rocky shores. The API is also sponsoring a study to develop a standard procedure for evaluating the performance of systems for controlling motor fuel vapor emissions at service stations. The latter study's object is to prove up a standard method for full evaluation of vapor emission control systems, which would also account for vehicle refueling losses.

The Votator Div. of Chemetron Corp. has sold two Votator-Schenk filters to help handle liquid radioactive waste. The waste-handling systems to be installed at power plants of Pennsylvania Power and Light and Niagara Mohawk Corp. were engineered by NUWCO, Inc., Sacramento, Calif., and Votator. The filter is a pressure leaf unit with horizontal plates in a vertical tank. According to Votator, horizontal units are not affected by process interruptions, as are vertical tube or leaf filters. The filter will discharge a dry cake with minimum liquid retention.

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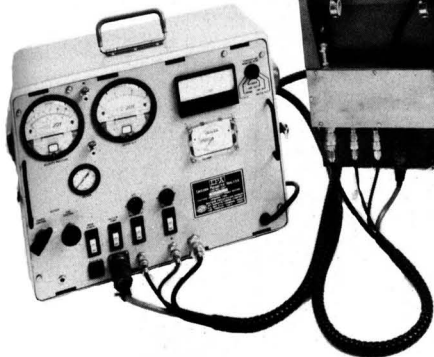
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Water pollution control industry

The wry, popular phrase, "good news and bad news," might be useful for any discussion of the water pollution control (WPC) industry this year. The good news—companies in this business can plan on material increases in sales and order backlogs, thanks especially to forthcoming federal requirements which, for municipalities, will also help to boost sales and order backlogs. Now, the bad news—shortages of materials and fuels and double-digit inflation and interest rates can severely cloud companies' financial structure and planning, despite rosy sales and order backlog prospects.

This special report discusses this industry in general; it also lists various individual companies, and describes their roles in the industry, as company spokesmen view them. The report also covers certain equipment suppliers and their trade association, WWEMA, as well as consulting engineering firms and technical experts, who generally make up the membership of the Water Pollution Control Federation (WPCF).

This team still stands ready, as it always has, to continue and accelerate progress in cleaning up the nation's vital resource—water. While sales in this field should continue to increase over the near term, the prospect of numerous companies' being able to perform their business according to scheduled time frames and cost estimates, and to turn a reasonable profit, may be uncertain. However, dollar volume of business (for which allowances for inflation should be made) will rise, and here is why:

- Just to achieve best practicable control technology currently available (BPCTCA) by July 1977, industrial interests will have to have devoted (1970–77) an estimated \$12.9 billion in capital costs alone (1971 dollars). The 1971 dollar capital cost increment necessary to attain best available technology economically achievable (BATEA) by July 1983 could be \$7.8 billion over and above the costs during the same interval.

- In its third annual report, the CEQ cited the need for expenditures of over \$86 billion for WPC for the period 1971–80. In its fourth annual report, the CEQ foresaw \$31.4 billion for capital investment, and \$30.4 billion for O&M; and \$54.1 billion for total annual costs, covering O&M and capital costs, over the period 1972–81. (On the other hand, as of July 1973, in its publication "Construction Review," The U.S. DOC foresaw wastewater expenditures at \$38 billion over the succeeding 10 years.)

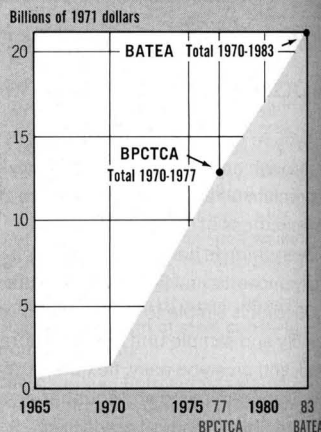
- According to a presentation by K. L. Kollar, director of the Water Resources and Engineering Program at the DOC's Bureau of Domestic Commerce, to the National Utility Contractors Association, at Boston, Mass., in April, construction put-in-place expenditures for municipal wastewater facilities (public and privately owned) were just under \$1.9 billion in 1972. These expenditures totaled nearly \$2.2 billion in 1973, and are expected to be about \$2.8 billion (1971 dollars) for 1975.

Business opportunities, such as may exist in times of economic adversity, will probably find financial support somewhere between the optimistic CEQ figures and the hard-fact, in-plant construction figures of the DOC. Account must be taken of funds promised by congressional and other sources, but undelivered; expected and potential cutbacks; and other uncertainties that lend a somewhat nightmarish quality to the lives of a company's financial officers. Probably, within this general, somewhat unsteady, framework, industry leaders see their business future.

Business operations

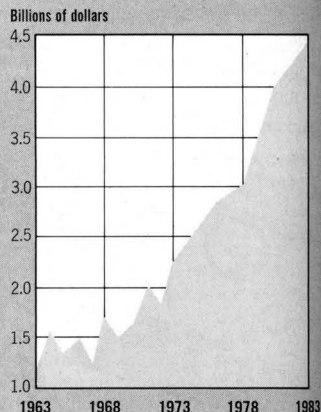
Many U.S. companies listed on stock exchanges or included in the over-the-counter market, or privately held, are devoting at least a portion of their operations to the wastewater treatment business. In many cases, these companies also engage in the companion business of water treatment. Many of them have their own

Industrial wastewater construction costs could skyrocket to comply with federal regulations



Source: DOC, Bureau of Domestic Commerce

Municipal wastewater construction outlays doubled in the past 10 years; could redouble in the next



Source: DOC, Bureau of Domestic Commerce

ES&T assistant editor Julian Josephson discusses a number of companies in this field, their products and services, and economic uncertainties some of these firms may face over the near term

in-house design engineering, equipment manufacturing, and construction capabilities. Such companies might even handle a whole array of wastewater treatment services and products for both industrial and municipal markets.

By comparison, other companies offer only one or two of the three capabilities previously mentioned. Also, some firms deal solely with municipal markets, while others concentrate on industrial markets. Whichever market they handle, however, over 300 companies are in this business of water cleanup.

Companies such as Peabody-Galton and Zurn Industries work in all sectors of the environment, including WPC. Envirotech deals with water and air. Others, such as Ecodyne and Dorr-Oliver, are solely in water and handle all three aspects of engineering, equipment supplies, and construction in the wastewater field.

Some companies take available water and make it satisfactory for industrial use. For example, the Cochran Environmental Systems division of Crane Corp., Infilco Degremont, Inc., and the Permutit division of Sybron Corp., to mention a few, handle this end of the business.

About two years ago (ES&T, November 1972, p 974), growth was forecast in both municipal and industrial WPC markets. With BPCTCA and BATEA to be required for industry, and some equivalent for municipalities, this prediction would seem to move toward fulfillment. Moreover, now, as in 1972, one would expect more rapid expansion of the WPC market in the industrial sector than in the municipal sector, since industries need not be delayed by financing arrangements such as municipal bonds, nor are they beset by vagaries of federal support.

Funds for industrial WPC, however, must come out of profits or new capitalization. The expenditure of these funds is considered to be generally unproductive; yet, in some industries such as paper or electroplating, among others, recovery and

reuse of materials in wastewater could materially mitigate the unproductiveness of funds spent on WPC.

Here are a number of companies actively engaged in the WPC industry, or some of its various aspects:

Ashbrook Corp., Houston, Tex., in this field for eight years, manufactures and markets high-speed aerators. In 1973, Ashbrook's sales were \$1.4 million, of which 95% were industrial and 5% were municipal. Ashbrook expects sales to be \$7 million for 1976, and \$25 million as a result of BPCTCA requirements.

Julius Tervay, Ashbrook's vice-president-marketing, considers long service and low maintenance costs to be the cost/benefit advantages of his company's mechanical surface aerators. He also feels that in addition to legislation, sales aggressiveness and the customer's moral obligations to the community motivate sales.

The company considers its best example of recent business to be the sale of about \$300,000 worth of aerator equipment to the Gulf Coast Waste Disposal District, Texas City, Tex. Starting in 1975, Ashbrook plans to offer on-line components.

Autocon Industries, Inc., a subsidiary of Control Data Corp., Minneapolis, Minn., has been in the WPC field for 50 years. Autocon's 1973 sales, of which 65% was for WPC, came to nearly \$9 million, compared with the previous year's sales of less than \$5.9 million, of which 62% was for WPC. Autocon's principal products for the field are meters and controls, of which 87% were sold to municipalities, and the remainder to industries.

Autocon projects 1976 sales to be \$10.5 million and, with BPCTCA in effect come 1977, \$12 million in sales are expected. The company considers a good example of its products at work to be on a municipal job at Iowa City, Iowa, where reduced power, chemical, and manpower requirements resulted.

The Resource Recovery Systems division of *Barber-Colman Co.*, Ir-

The 21 WPC equipment categories

- Aerators
- Chemical feeders
- Chlorinators
- Combination units
- Degritters
- Dewatering, incineration, wet combustion
- Digestion
- Filter rate control, filter gauges, wash troughs, distributors
- Filter underchains
- Flocculators
- Ion exchange units
- Meters and controls
- Mixers
- Pressurized flotation
- Pumps
- Screens and disintegrators
- Sedimentation
- Wastewater package pumping stations
- Wastewater package treatment plants
- Water package treatment plants
- Water quality monitoring

Useful abbreviations

- BATEA**
Best available technology economically achievable
- BOD**
Biological oxygen demand
- BPCTCA**
Best practicable control technology currently available
- BPT**
Best practicable treatment
- CEQ**
Council on Environmental Quality
- DOC**
Department of Commerce
- EPA**
Environmental Protection Agency
- O&M**
Operation and maintenance
- RO**
Reverse osmosis
- SS**
Suspended solids
- WPC**
Water pollution control
- WPCF**
Water Pollution Control Federation
- WWEMA**
Water and Wastewater Equipment Manufacturers Association

vine, Calif., is offering its Puretec system which, among other things, will help to recover metal and chemical values from sewage sludge (*ES&T*, August 1974, p 703). As of June, this system was being piloted in Orange County, Calif., and in Philadelphia, Pa.

Calgon Corp., Pittsburgh, Pa., a subsidiary of Merck & Co., Inc., continues to market a number of products and services in WPC and water reclamation. As in 1972, Calgon's major sales items are still water treatment polymers and granular activated carbon for water purification and WPC.

The Calgon Adsorption Service for wastewater treatment, established about September 1972, is coming into increasing use. With this service, organic content is reduced by passing wastewater through columns of activated carbon. According to Calgon, this process avoids large initial capital investment costs associated with other approaches. Calgon now has about 12 of these service systems in use by customers, as well as a multiple hearth regeneration facility for carbon reuse.

Calgon expects to expand its granular activated carbon capacity by over 50 million lb/yr, at a total cost of about \$31 million. About one half of this expansion will take place at the company's facility in Cattelburg, Ky.; the balance will be at a new plant at Feluy, Belgium.

Carborundum Co., Niagara Falls, N.Y., will market granular activated carbon made by a new, proprietary process (*ES&T*, August 1974, p 691). Carborundum hopes to complete a semicommercial plant at the end of this year, capable of making several hundred thousand lb/yr of the material. By the end of 1976, Carborundum hopes to complete a \$10-million, full-scale granular activated carbon plant.

The *Carus Chemical Co.*, La Salle, Ill., is a privately held company that manufactures a chemical for the municipal water and wastewater field. This aspect of Carus' efforts constitutes about 20% of the company's total business.

In 1959, Carus started selling its chemicals for water treatment; about 10 years later, marketing chemicals to the wastewater field began. The company estimates that its market in potable water treatment was built up entirely through marketing and sales efforts, and the governmental regulations had little or no effect. By contrast, governmental regulations had a significant effect on sales of the company's chemicals to the wastewater treatment market.

Now 96 years old, *Clow Corp.*, Oak Brook, Ill., had net sales of over

\$116 million compared to about \$97 million in 1972.

This year, Clow offered a new PVC plastic gravity sewer pipe with an integral polyurethane push-on Deflec-Tite joint; the pipe is offered in diameters of 4-12 in. and lengths of 13-20 ft. According to Clow, the pipe is installable at lower than conventional costs, and can control infiltration and exfiltration to low limits. The first installation (municipal) of this pipe was made in Florida in February.

Clow also introduced a new use for a proved product by employing Clow-Yeomans "Shone" sewage ejectors (air pumps) for removal of scum from clarifier tanks. This approach is considered by the company to be superior to more conventional alternate pumping systems. The Metropolitan Sanitary District of Greater Chicago is using 58 of these ejectors.

Crane Co., New York, N.Y., a large firm heavily involved in the WPC field, reported sales of \$947 million in 1973, up from \$844 million the previous year.

In 1972, spokesmen of Crane's Cochrane Environmental Systems division, King of Prussia, Pa., believed that increasing emphasis on pollution

control by municipalities and industries would lead to future sales. This belief has been largely justified. Crane services the electric generating industry and the pulp and paper industry, as well as other WPC markets.

Degremont, Inc. (formerly in Liberty Corner, N.J.) recently acquired the assets of the Infilco division of Westinghouse, and dissolved Degremont's relationship with Gulf. The new corporate name, as of May, is *Infilco Degremont Inc.*, Richmond, Va., and the Liberty Corner, N.J., operation of Degremont has been closed. Degremont personnel were transferred to the Infilco offices.

Infilco Degremont's business is split about 50-50 between municipal and industrial. The company does its own design engineering, but does not provide outside consulting services. About one third of its business volume comprises wastewater treatment equipment. Occasionally, the company will take on systems jobs in which it furnishes the entire line of equipment necessary, even though the company might not manufacture all of the equipment; it is doing a \$1.5-million project of this type. However, the company does not do turn-key projects. Its wastewater

Economic clouds over the WPC industry

The economic tempest in the U.S. today has outgrown its proverbial teapot by a few orders of magnitude, and it is making its effects felt on the water and WPC industry. Major problems appear to be availability of various necessary commodities and the lead time for obtaining them, serious price inflation, and unprecedented costs of borrowing money where money is indeed available for loans. It is impossible to predict when relief may come, particularly since a clouded economic picture coexists with an unsettled domestic and international political situation as this goes to press.

Company comments

ES&T asked various companies if the energy crisis, tight money situation, or both affected business or sales in any way. A few companies said "no"; perhaps perspicacity, management, good fortune, a fortuitous position, or some combination of these factors put such firms in the enviable situation of being insulated against an adverse economic climate.

Other companies are feeling the bite, however. One company told *ES&T* that delivery lead times and profits were adversely affected. These problems are apparently exacerbated by the double-digit cost of money, the difficulties municipalities are experiencing in floating bond issues, and postponement of projects on the part of industry and local governments—again, because of high money costs. Impoundment of funds appropriated to the EPA adds icing to the cake.

In some cases, companies told *ES&T* that they cannot buy, on the open market, types and quantities of raw materials needed to operate their plants at or near 100% capacity, particularly where fabrication is involved. In this respect, steel, for example, is a difficult commodity. Where steel and other necessary materials do become available, their prices are often unstable.

Changing numbers

Perhaps the most disturbing situation involves rapidly changing numbers—that is, dollar price quotes upon which a purchaser cannot rely. This situation affects all aspects of supplies to WPC companies, WPC company operations, and industrial, municipal, and federal markets for their products and services.

On the industrial side, WPC companies' customers find that capital, needed for WPC installations, is either unavailable or extremely costly, and these customers often find themselves driven to postponing or canceling WPC projects. For the same reason, as well as because of difficulties in obtaining materials, the WPC companies cannot expand capacity to meet orders, and severe delays in deliveries to customers frequently result.

On the municipal and federal sides, contracts between the municipality or agency, and the WPC company are made according to bid; sometimes provision for cost overruns, "within reason," are written into the contract. The wild nature of the present inflation, however, is such that skyrocketing cost increases could

treatment plant for the state hospital at Foxboro, Mass., for which the company supplied equipment, is a good example of an Infilco Degremont demonstration project.

Dravo Corp., Pittsburgh, Pa., chalked up revenues of \$415.5 million in 1973, as compared to \$378.8 million in 1972. Involved in WPC, Dravo's Process, Construction, and Engineering division, accounted for \$117.5 million of the \$415.5 million total.

Dravo completed a wastewater treatment facility for Atlantic Richfield Co. at Philadelphia, Pa. The company was also working on a similar project for Getty Oil Co. in Delaware, and a multiwastewater treatment plant for Dominion Foundries and Steel, Ltd. (Canada). Dravo is installing its Denite system for removal of nitrogen nutrients from sewage in Florida and other Atlantic Coast states.

Dravo received a \$4.5-million order to design, build, and install a secondary waste treatment system for the Gulf Coast Waste Disposal Authority, Texas City, Tex. This facility will remove oil, SS, and BOD from wastewater at an Amoco Oil Co. refinery and an Amoco Chemicals Corp. plant at Texas City. A similar

order was received for a New Jersey refinery. Dravo also booked a major water management study order from a Weyerhaeuser Co. paper mill in the state of Washington.

Dorr-Oliver Inc., Stamford, Conn., in business for well over 50 years, provides systems and equipment for wastewater treatment to cope with municipal and selected industrial problems. For 1973, the corporation recorded net sales of about \$93 million.

While involved with industrial application, the bulk of the company's wastewater treatment business is municipal. From the process standpoint, *Dorr-Oliver's* approach utilizes centrifugal thickening of activated sludge, heat conditioning, centrifugal dewatering and fluid-bed combustion.

Ecodyne Corp., Chicago, Ill., posted 1973 sales at over \$96.3 million, a 26% increase over 1972 sales of \$76.5 million. Both years broke records. Of \$89.8 million of these total 1973 sales, industrial sales were about \$30.9 million, electric utility sales \$29.2 million, municipal sales \$15.2 million, and residential and commercial sales almost \$14.5 million. *Ecodyne*, 85% owned by Trans Union Corp., claims to be the largest diversified company devoted exclusively to water and wastewater treatment, and water cooling.

In October 1973, *Ecodyne* acquired a Canadian subsidiary, *Adam Clark Co., Ltd.*, Hamilton, Ont., which provided *Ecodyne* the ability to expand its turn-key industrial and municipal wastewater treatment business in Canada and elsewhere. Sales listed above for *Ecodyne* do not include those of *Adam Clark*.

The Smith and Loveless division of *Ecodyne*, Lanexa, Kan., has been in the municipal end of the WPC field and related fields since 1946. The division sold eight WPC items during 1973 for a total of \$13.3 million. Division WPC sales were \$11.2 million in 1970, and are projected at \$18.8 million for 1976. For 1977 BPCTCA requirements, the division foresees sales of \$21.7 million.

This *Ecodyne* division has an in-house consulting, design, and engineering staff, and its Kansas facility does municipal WPC business exclusively. The division feels that the best recent example of its work was a tertiary filter system for a wastewater treatment plant at Naperville, Ill. The project value was \$1 million.

With sales near \$241 million for its fiscal year ended March 31, 1974, *Envirotech Corp.* (Menlo Park, Calif.) markets a broad line of equipment, processes, and expertise for both industrial and municipal water and wastewater treatment. WPC sales came to \$139.1 million. The compa-

ny, in business five years, seeks to maintain a minimum growth in per-share earnings of 15%/yr.

Envirotech supplies a multiplicity of on-line analysis, monitoring, and control systems. The firm also offers BPT equipment of various sorts, as well as 15 of the 21 lines of wastewater products (see box). Among cost/benefit advantages realized from *Envirotech's* BPT equipment, according to the company, are:

- utilization of on-line analysis, monitoring, and control systems to optimize or reduce O&M costs required to operate a plant
- employment of a plural-purpose furnace to burn sludge and reclaim lime simultaneously for reuse in a variety of applications
- utilization of a heat treatment system or pressure filtration system prior to incineration to reduce further energy costs of incineration which, according to *Envirotech*, studies are shown to be only 60% of such costs for land disposal around major metropolitan areas.

Envirotech does not offer consulting services as such; however, the firm advises customers on technology, use, installation, and operation of conventional and advanced design equipment. The company does not do turn-key installations, but it does furnish equipment or technological assistance to a consulting engineer or contractor.

Envirotech lists as most recent showcase examples of its construction advanced WPC systems for the City of Hillsboro, Ore., and at Lower Allen Township, Pa., Granite City, Ill., and Hampton Roads, Va. These systems, furnished by *Envirotech's* Eimco BSP division, often feature energy savings, and, sometimes, resource recovery. As for instruments and controls, *Envirotech* looks proudly at an \$80,000 installation for the City of Tallahassee, Fla.

Gelman Instruments Co., Ann Arbor, Mich., manufactures and markets instruments and materials for biological water testing that are not used on-line. The company has in-house microbiologists and technicians who perform on-site training. Sales in 1973 were more than \$7.4 million, up from \$5.6 million the previous year.

The company is not involved directly in turn-key installations, but it does work through organizations representing manufacturers to sell all equipment for a turn-key laboratory. *Gelman* supplied 200 such concerns in 1973, and expects to have supplied 400 by the close of this year. The company's business is 80% municipal, and 20% industrial and feels that the technical support it provides

well erase a successful bidder's profits, and leave the contracting company with a loss, despite the cost overrun clause, by the time the contract is fulfilled. Indeed, it is not always certain that under present economic circumstances, a given WPC company would be financially able to complete its contract, which may explain why a number of firms could have become leery of bidding lately.

Escalator clauses

To obtain relief, companies may seek escalator clauses in their contracts, which allow them to charge their customers extra as their own costs rise. Some companies have asked escalation provisions of 15-20%; in a northern state, one company told a municipality, "50% or no bid." Certain states, such as Massachusetts, New York, and Washington now have, or are considering, legislation which would provide for escalation funding. However, no organization—industrial, municipal, state, or federal—providing funds wants to see its dollars disappear into a bottomless pit and, simultaneously, further fuel inflation.

At the same time, the WPC companies understandably want business, but not on a basis on which most jobs incur losses. Thus, they are, in a sense, caught between Scylla and Charybdis, with a number of them in, or approaching, serious financial straits. Unfortunately, no quick-fix solution to the changing numbers problem has been proposed—one probably cannot be—but if some workable approach is not soon forthcoming, the program of water pollution abatement in our nation could be severely impaired.

to perform biological tests required by legislation motivates sales.

BIF, a unit of *General Signal Corp.*, offers flow meters, sewage grinders, sludge stabilizing and conditioning equipment, and related products, as well as integrated, entire WPC systems. The company either designs the system or works with a consulting engineer. BIF recently put into operation a half-million-sq-ft wastewater treatment equipment facility at West Warwick, R.I., to meet demand.

Leupold & Stevens, Inc., Beaverton, Ore., is a privately held firm which makes water-level recorders and total flow meters used in monitoring open channels. The company holds sales figures confidential; however, sales of products doubled from 1971 to 1973; and the company foresees another doubling by 1976. Leupold's markets are one-third municipal and two-thirds industrial, and are serviced through manufacturer's representatives.

Leupold & Stevens has been in the water resources field since 1911, and in measuring wastewater flows since the 1930's.

Met-Pro Water Treatment Corp., Lansdale, Pa., achieved a sales volume of about \$5.8 million for its fiscal year ending January 31, 1974, up 74% over the prior year. During the past two years, sales of advanced sewage treatment systems have begun to "take off" and sales of fiberglass pumps for handling corrosive fluids have increased "dramatically," according to the firm. Met-Pro has also accelerated its marketing of waste treatment and filtration equipment for the electroplating and metal finishing industries.

Met-Pro now has an International division, and representation for products in some European, Caribbean, and South American countries, in addition to its original five divisions (*ES&T*, November 1972, p 976-77).

Neptune International Corp., Atlanta, Ga., is involved with treatment plants for water purification, tertiary treatment processes for wastewater reclamation, chemical feeders, dewatering equipment, heat treatment systems, sludge incinerators, treatment plants, and related items. The company's total sales for 1973 were \$77.2 million, compared to 1972 sales of 67.2 million. Of the 1973 sales, 42% stemmed from WPC, as compared to 35% from WPC during 1972. In the WPC field, Neptune's sales were over \$15.6 million in 1970, and nearly \$23.8 million in 1973 for seven WPC items; and projected WPC sales for 1976 are \$56.5 million.

Neptune has its own design staff, but does not offer on-line compo-

nents or consulting services. The firm is involved with turn-key projects "very little." Of Neptune's products and services, 75% go to the municipal market, and 25% to the industrial market. Neptune's subsidiary, *Nichols Engineering and Research Corp.*, has been in the wastewater business since 1934.

Osmonics, Inc., Hopkins, Minn., has been in WPC since its founding in 1969, and claims to be the first company to promote RO for industrial waste treatment. About 40% of Osmonics' sales are in WPC, and such sales were \$300,000 in 1973, up tenfold from 1970 figures. For 1976, Osmonics' president D. Dean Spatz projects sales of \$1-1.5 million. The company offers on-line components and services for industrial systems.

According to Osmonics, most of its BPT equipment pays for itself through saving reusable products. Spatz sees paybacks of capital and operating costs in less than one year for nickel or sugar reclamation, and three years or less for most other applications.

Osmonics does its own engineering for most installations, but may work with a customer's engineers, or, on larger jobs, with independent consultants on a specific job basis. All jobs that Osmonics does are in the industrial market. The company offers turn-key installations, since its equipment is usually part of a total turn-key job, is of a packaged nature, and requires little on-site labor. Osmonics expects "a couple of turn-key jobs a year."

The company considers a typical model installation to be similar to the Rock Island Arsenal (Ill.) system, done together with *DMP Corp.* (Charlotte, N.C.) as a turn-key job.

WPC accounted for about 35% of the sales of *Parkson Corp.*, Fort Lauderdale, Fla., in 1973, and is expect-

ed by the company to reach 65% this year. The company offers Lamella gravity settlers (sedimentation equipment), as well as flocculators to interface with their gravity settlers. Parkson expects 1976 sales to sextuple those of 1973. Industry accounts for 90% of Parkson's market; the remainder is the federal government.

Parkson designs its own equipment, and feels that capital cost savings of up to 40%, size reduction of up to 95%, elimination of moving parts, and (in a few cases) selling recovered solids help to motivate Parkson's sales.

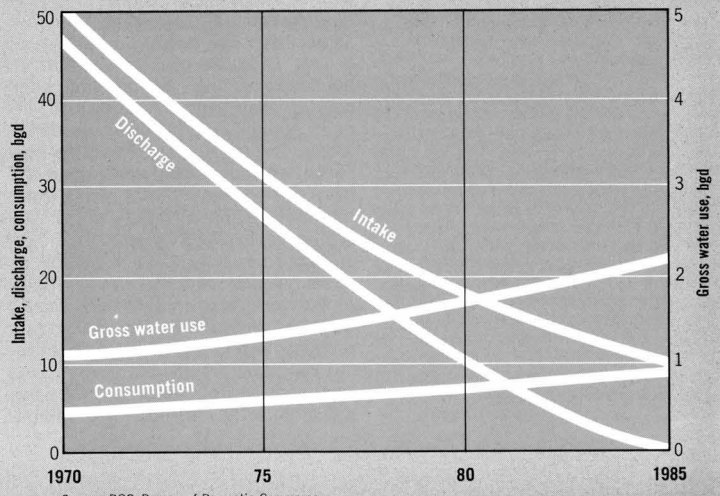
Parkson lists jobs done at Carpenter Steel (Reading, Pa.), and a \$100,000 Lamella installation at U.S. Steel's Agrichem division (Atlanta, Ga.) as models. A "conventional" settler would have cost \$160,000.

Peabody-Galion Corp., New York, N.Y., an across-the-board environmental company, reported sales of nearly \$183 million in 1973, as compared to \$144.8 million in 1972. The water group (WPC and municipal sewage) accounted for 19% of 1973 sales, or about \$34.6 million a 10% increase over 1972.

Peabody markets a large WPC product line through a multimarket distribution organization, and full WPC systems through a central sales engineering staff. Through these groups, Peabody reported sales of over \$25.6 million worth of water-handling and -treatment equipment, and \$8.9 million for plant construction and installation in 1973. During that year, Peabody was constructing major wastewater treatment plants in Florida, Illinois, Massachusetts, North Carolina, Puerto Rico, Rhode Island, and South Carolina.

Sewer collection, maintenance, investigation, and rehabilitation products and services also are important to the WPC industry, and *Penetryn International, Inc.*, Latham, N.Y.,

Industrial water use at "no discharge"



sold \$7.5 million worth of these items in 1973; total 1973 sales were \$9.5 million. In 1970, the sales of these items totaled \$4 million, and are projected at \$10 million for 1976. About 75% of its business is municipal and government, and 25% contractor, industrial, and utility. Penetryn considers its best example of recent work to be a job of cleaning, inspecting, testing, and sealing sewers at Grove City, Ohio.

Pennwalt Corp., Philadelphia, Pa., reported 1973 sales of over \$500 million. About 9% of those were to environmental cleanup markets. The company's Sharples Stokes division is making and marketing solid bowl centrifuges, including a new Super-D-Canter centrifuge for such difficult jobs as secondary sludge separation without the use of chemical polyelectrolytes. As of March 31, the order backlog for centrifuges was close to \$30 million.

Rexnord Inc., Milwaukee, Wis., formerly Rex Chainbelt, Inc., posted sales of \$442 million for 1973, as compared to \$363.5 million for 1972 (fiscal year ending October 31). Rexnord's Envirex Inc. subsidiary, which deals with environmental control equipment, accounted for \$31.5 million of the 1973 sales. The Water Quality division of Envirex chalked up about 70% of Envirex sales.

During fiscal 1973, the Environmental Services division of Envirex put in a biological and a chemical pilot treatment plant at Kenosha and Racine, Wis., both lakeshore communities. These communities were under state requirements to separate sanitary and storm sewer systems physically. The Envirex systems, according to the company, handle the problem with large savings to the taxpayers, since the Envirex systems obviated the need for parallel sewer system. The Envirex systems started up in June 1973, and Envirex says that an industry "first" was accomplished.

Sterling Drug Inc., New York, N.Y., reports 1973 sales of over \$864 million. Its subsidiary, Zimpro, Inc., ended 1973 with an order backlog of \$28.1 million for WPC systems and equipment. Zimpro came into being to exploit a patented wet air oxidation process for industrial and municipal WPC. This process grew out of Sterling's expertise in extracting valuable by-products from black liquor—dark liquid waste from paper mills.

Zimpro's business is 90% municipal and 10% industrial. Most of its installations are turn-key (11 done in 1973), and capabilities for consulting, design, and engineering are in-house. Sterling, through Zimpro, has been in the WPC business 16 years.

United States Filter Corp., New

York, N.Y., posted sales of \$162 million for 1973, as compared to over \$123 million for 1972. U.S. Filter's WPC group received a major contract from Texaco to engineer and build multimillion dollar wastewater treatment facilities to handle 3.8 million gpd of wastewater at Texaco's refinery at Port Arthur, Tex. U.S. Filter's Drew Chemical subsidiary, which manufactures and markets water and wastewater treatment chemicals, increased its first quarter sales for 1974 30% over the same period of 1973.

Zurn Industries, Inc., Erie, Pa., is a total environmental company. Since its founding in 1900, it has always dealt with wastewater treatment. Zurn offers both software (environmental and engineering services) and hardware (products and services) items.

For the fiscal year ended March 31, 1974, Zurn's net sales were almost \$205 million. Environmental systems and services as a whole accounted for 66% of these sales, and WPC alone, 26%. For the 1973 fiscal year, net sales were almost \$196.6 million, with environmental equipment and systems accounting for 61% of these net sales. WPC sales comprised 40% of Zurn's environmental sales for that fiscal year.

Zurn is building a pair of waste heat energy recovery systems for the \$47 million Central Contra Costa wastewater reclamation facility at Concord, Calif. This plant will recycle 30 million gpd of municipal sewage. The Zurn systems will convert waste gases into steam energy (70,000 lb/hr total), so that plant emissions to the atmosphere would be clean.

At the end of their fiscal 1974, Zurn's order backlog was \$70 million for environmental work, up from \$56 million the previous year.

Consulting engineers

As a general rule, construction firms in the industrial area, in addition to private consulting engineers, handle all phases of a contract—engineering design, equipment purchase and supply, and construction. Generally, the bigger the job, the greater the tendency to use construction firms. In the municipal wastewater treatment area, however, consulting engineers normally prepare a plant design for a municipality, and then contractors bid competitively for construction based on the consultant's design.

Fundamentally, the consultant prepares the design and specification. Usually, he also specifies equipment, supplies, and processes for new construction projects, as well as extensions and replacements. However, some municipalities operate depart-

ments whose engineers prepare design plans and supervise construction. In many cases, these municipal engineers work with consulting engineers.

Technical associations

Founded in 1928, and with a membership of about 23,000 the WPCF, Washington, D.C., is the technical association devoted exclusively to problems of WPC. Its members have the responsibility for technical detail and equipment specification for the construction, operation, and management of wastewater collection and treatment systems.

There are 63 so-called WPCF federation member associations in the U.S. and Puerto Rico, and abroad. These suborganizations deal with promotion, management, design, financing, and operation of facilities for WPC through proper collection, treatment, and disposal or reclamation of domestic and industrial wastewater.

WWEMA, Newark, N.J., operating since 1908, is the trade association for over 300 equipment manufacturers and suppliers in the U.S. WWEMA now sponsors equipment exhibits and technical meetings. Its most recent meeting was held in Detroit, Mich., in early April, and covered a variety of WPC equipment topics (*ES&T*, June 1974, p 513-14).

Jean Donohoe, WWEMA's public relations manager, says that the association, looking to the future, will sponsor another equipment show and meeting next April 2-4 in Chicago. The show and meeting will be aimed at industrial users of such equipment.

It is not surprising that the largest portion of expenditures for a wastewater treatment plant goes for concrete, brick, mortar, labor, and the like. Equipment may account for less than 20% of the total cost for such plants, and even less than 15% in the case of primary sewage treatment plants.

In *ES&T's* report of 1972, water and WPC equipment were grouped into 21 items in a manner devised by DOC's Kollar. He compiled in-plant shipments of equipment in both the water and the WPC fields (*ES&T*, November 1972, p 978). The list of such equipment is repeated (see box); however, DOC has not yet updated its WPC and water industry survey.

For a list of individual companies that supply one or more of the specific 21 items, the reader is referred to the 1974-75 *ES&T* Pollution Control Directory. The Directory is available from American Chemical Society Special Issues Sales, 1155 16th St., Washington, D.C. 20036.

OUTLOOK

Environmental laboratories

Some have come together to ensure the integrity of their profession

With the creation of stringent environmental standards, a myriad of private environmental laboratories have sprung into existence, making their analytical services available to industry and to governmental agencies. This is not an uncommon phenomenon. Anytime a new market is opened, any number of independent business operations will arise to serve that market. Many times the quality of such services take a back seat, most probably from inexperience and the intent to make a fast buck.

Browsing through available lists, one could find several hundred laboratories that claim to be in the environmental analysis business. How many of these are truly capable of rendering high quality service?

Obviously, the question was raised in the minds of people involved with the environmental laboratories. A group of such people, concerned with their professional image and the existence of possible "fly-by-night" operations, have come together to form the Association of Environmental Laboratories (AEL), with headquarters in Schenectady, N.Y.

Activities

Incorporated in December 1973 as a nonprofit organization, AEL consists of 12 charter members under the leadership of James Setser of Environment/One Corp. The association began its membership drive this summer, offering full membership to laboratories selling their services on a profit venture basis. Industrial laboratories which buy services and also operate their own laboratories are invited to become associate members.

Dues are \$150 annually for each type of membership. There is no confinement with respect to the size of the laboratory. It's the quality that is significant. The fundamentals of "quality" include the existence of an actual laboratory with trained personnel and management, a well-executed quality control program, and good record-keeping practices. This last criterion runs the gamut of—repro-

ducible methods of receiving samples, logging, storage, analysis, and documentation—so that there will be no possibility of sample mix-up, contamination, and aged results. In other words, the laboratory is not a mere storefront operation which farms out the analyses.

One of the early goals of the association will be to provide substantial input to the Environmental Protection Agency or its selected contractor in the development of certification programs for private environmental laboratories. According to Setser, certification of laboratories has heretofore been restricted to an "approved list of laboratories" in a few individual states, and inspection-control programs have not been employed to ensure that the laboratories are actually qualified. The generation of inaccurate data by unqualified laborato-

ries, he said, could result in serious legal ramifications for industries who must file discharge monitoring reports under the National Pollutant Discharge Elimination System.

Capabilities

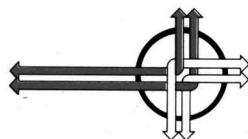
A large number of separate laboratories are operated throughout the U.S. by AEL members. Five of the charter members (AWARE, Calgon, U.S. Testing Co., NUS, and Ryckman & Associates) offer design engineering and pollution abatement services in addition to analytical services. Of particular interest is Raytheon's involvement in modeling open ocean currents and estuaries and siting nuclear power plants, ERG's study of the ir

Michigan (ES&T, July 1974, p 598) and river quality in Michigan's upper peninsula. LCC

AEL at a glance

Emblem

Egyptian symbol of unity—bound arrows within a circle, signifying the various capabilities of the members tied to common goals

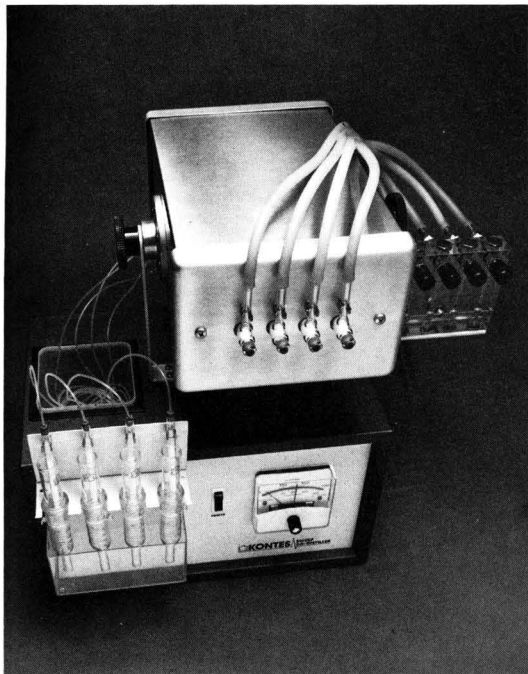


Charter members

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(D. Bassett)
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(R. N. Corning)
Crobough Laboratories, Inc.
(M. L. Levy)
Environment/One Corp.
(J. Setser)
Environmental Research Group, Inc.
(F. Hammer)
Environmental Triple S Co.
(D. Vornberg)
NUS Corp.
(J. K. Rice)
Raytheon Co.
(G. Cox)
Ryckman, Edgerley, Tomlinson
(D. W. Ryckman)
Suburban Laboratories, Inc.
(E. I. Rosenberg)
U.S. Testing Company, Inc.
(E. Rider)
AWARE, Inc.
(W. Eckenfelder)

Goals

- establish, maintain, and promote a professional status for laboratories in the field of environmental measurements
- establish standards of excellence and code of ethics for these laboratories
- establish an information retrieval system for measurement techniques for members
- maintain a system of rigid quality control among members
- adopt and maintain established and recognized analytical procedures for environmental analyses
- maintain liaison with governmental laboratories in establishing acceptable "standard" analytical procedures for environmental analyses
- promote educational guidelines for training of analysts and technicians
- take a position of leadership in promoting reliable environmental definition programs
- provide a "round robin" evaluation program for new analytical procedures



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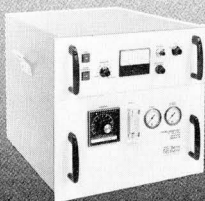


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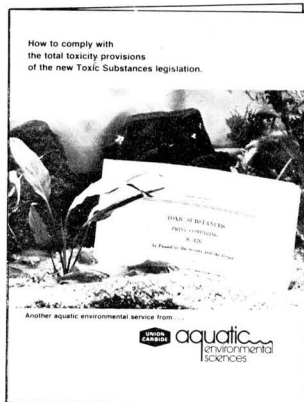


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A shortcut to the determination of effluent quality and design of full-scale facilities

Wastewater treatment: a pilot plant on the move

The word in the physical-chemical wastewater treatment business these days is mobility—mobility in terms of compaction, and cutting down on expenditures, time, manpower, and energy. This sort of convenience comes in the form of a one-truck trailer which can be hooked up to any type of primary or secondary treatment system to collect data for physical-chemical treatment of raw sewage or primary effluent, or to further treat effluent from biological processes.

The mobile van demonstrates that a given process can provide an effluent of specified quality. It also functions as a pilot plant from which data can be used for direct scale-up to full-size equipment and systems. There are three companies who own such physical-chemical treatment vans—Envirex Inc. (a Rexnord company), Envirotech Corp., and Hydromatation Filter Co.

Parameters measured

Each of the vans, with a treatment capacity of about 25,000 gpd, essentially investigates the same design parameters. Envirex's equipment, for example, contains provisions for:

- chemical coagulation and flocculation—types and dosages of chemicals for optimum removal of phosphorus, BOD, and suspended solids
- sedimentation—settling velocities, overflow rates, and detention times required for full-scale clarifiers; volume and character of sludge produced
- sand filtration—types and dosages of chemicals to improve filter performance; optimum backwash rates; head loss requirements

- carbon adsorption—required contact time; substitution of activated carbon with ion exchange materials for ammonia (ammonium ion) removal.

With these and other features, and about 250 flow patterns, Envirex can work up more than 1000 different schemes for municipal and industrial waste treatment plants. In addition, the equipment and piping arrangements in the van enable the optimum choice of chemical pretreatment, such as the addition of lime (one of two stages), ferric chloride, alum, polyelectrolytes, sodium aluminate, or waste pickle liquor.

Rental agreement

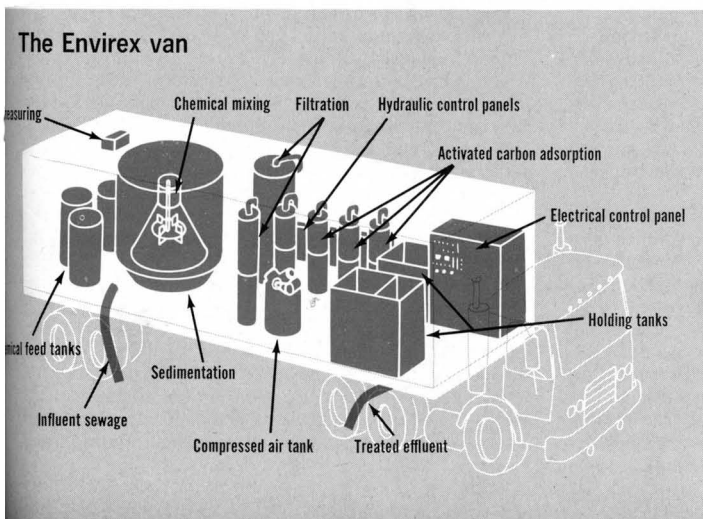
All of the vans come with a service operator who works a 40-hr week. For each flow scheme, there is instrumentation for pH, pressure (head loss), and flow. However, analysis of collected samples for BOD, COD, TOC, suspended solids, and other parameters is the renter's responsibility. The renter also pays for transportation of the van, the chemicals used, and utility charges. On the average, the monthly rental fee runs about \$10,000.

Applications

Envirex, the newcomer in this field, launched its van in April at Waukesha's (Wisconsin) secondary trickling filter sewage treatment plant. Chemical treatment with lime and tertiary dual media filtration before carbon adsorption have been tested to improve the quality of the final effluent which empties into the Fox River, on the borders of Chicago. This van, expected to complete its first tour this summer, will then be available to other clients.

Envirotech's van has been around for 2½ years and has been leased to municipalities in California. A spokesman said that various housing developers have expressed interest in the van. Their intention is to use the van as a miniature treatment facility for the first residents while the housing project is undergoing completion. Envirotech is willing to custom make these vans for those wishing to buy and not to rent.

Unlike its competitors, Hydromatation Filter recommends only proprietary equipping. With five years of van experience in tow, the company is a bit disheartened about rental prospects. LCG



FEATURE

When completed and with more advanced wastewater treatment processes than any other facility, the Blue Plains plant in Washington, D. C., easily wins the title of the . . .

"Largest advanced wastewater treatment plant in the U.S. and in the world"

Donald E. Schwinn

Stearns & Wheeler, Cazenovia, N.Y. 13035

George K. Tozer

Metcalf & Eddy, Inc., Boston, Mass. 02116

In June 1968, the District of Columbia (D.C.) retained Metcalf & Eddy (Boston, Mass.) to examine the District's Blue Plains Water Pollution Control Facility. The study, completed in February 1969, recommended the immediate expansion of additional secondary treatment facilities to remove 90% of biological oxygen demand (BOD) and suspended solids (SS), for an average flow of 309 mgd, with provisions for future expansion to 419 mgd and for nutrient removal. These provisions, requiring reclamation of 51 acres of Potomac River mud flats, raised opposition from the Department of Interior at the April 1969 Potomac River Enforcement Conference (PREC). After several months of debate, the Department of Interior and the local jurisdictions signed an agreement limiting the site capacity to 309 mgd and calling for a second regional plant in suburban Maryland.

The 1969 PREC established treatment requirements among the strictest in the nation. The conference proceedings incorporated an implementation schedule for completion of the entire project, including nutrient removal, by 1977. However, in 1970, the Department of Interior requested a construction schedule to provide that all facilities be in operation by December 31, 1974. To meet this schedule, it was essential that all processes for secondary and advanced wastewater treatment be selected by July 1971 and that the design of all facilities be completed by October 1972.

In 1970, the joint Environmental Protection Agency-District of Columbia (EPA-DC) pilot plant located at the Blue Plains Water Pollution Control Plant was significantly expanded to permit the evaluation of a number of new secondary and advanced treatment methods potentially applicable to meet the new Potomac River criteria.

In July 1971, Metcalf & Eddy recommended and the District of Columbia adopted the modified-aeration activated sludge process, upgraded to near 90% BOD and SS removal by the addition of alum or ferric chloride. Other recommendations included:

- nitrogen removal by the biological nitrification-denitrification process, consisting of nitrification and denitrification reactors and sedimentation basins
- phosphorus removal by the addition of alum and/or ferric chloride to both the secondary modified aeration system and to the denitrification system; filtration and disinfection of the effluent from the denitrification system before discharge to the river
- sludge processing by gravity thickening of primary and stormwater sludges, flotation thickening of secondary and advanced treatment sludges, followed by vacuum filtration and incineration.

Selection of these key process steps in July 1971 was based on a composite of testing at several locations in the U.S., but the system had not been piloted in its entirety in D.C. Since then, the design has proceeded concurrently with confirmatory tests at the EPA-DC Pilot Plant on D.C. wastewater. This testing program not only demonstrated the high reliability of the recommended processes, but also provided valuable information on design and operating features which have been incorporated into the project.

Implementation progress

Because of the subsequent delays in authorization of grant funds, completion of construction, originally scheduled for December 31, 1974, has been delayed until 1978. The project, with an estimated cost of \$360 million has been subdivided into approximately 20 contracts. Detailed engineering design of plant components has been divided into several parts, with Metcalf & Eddy responsible for the design of the liquid treatment facilities and Whitman-Requardt Associates (Baltimore, Md.) for the solids processing facilities. Since three years were originally anticipated to complete the entire \$360 million project, it was decided to perform all excavation and site preparation in a single contract, rather than as part of each individual contract. This contract included the excavation of 3.5 million yd³ of material, and dewatering and partial sheeting of the site. The excavation has been fully completed.

In February 1972, bids were received for interim chemical feed facilities to feed either ferric chloride or alum to the existing modified activated sludge secondary facilities for reduction of load on the river while the new facilities were being designed and constructed. The PREC's request, that these facilities be in operation by May 1972, was fulfilled with significant improvement in effluent quality. Construction of additional primary treat-

ment facilities to expand peak capacity from 300 mgd to 939 mgd was completed this August.

During the initial construction planning phase, Metcalf & Eddy recommended that D.C. build a large docking facility to facilitate shipment of bulk construction materials and equipment. This dock would be used for receiving bulk shipments of chemicals and for removal of sludge ash when construction is completed. Accordingly, Metcalf & Eddy designed a docking facility for which construction is now complete. The dock is 1200 X 100 ft, consisting of prestressed concrete slabs. It is a free-standing structure and can accommodate a concrete plant. Piping is included to receive shipments of chemicals such as alum, ferric chloride, methanol, and fuel oil. A channel has been dredged to the dock site, a distance of approximately 2000 ft.

For the construction phasing process to permit operation of the new secondary facilities by the fall of 1974, an interim secondary effluent conduit contract was awarded. Bids for construction of additional secondary treatment facilities were opened in December of 1972. Construction is now under way and includes modifications to the existing secondary system, and construction of new secondary reactors and sedimentation basins. Completion date for this contract is set for July 1975. Design of instrumentation systems for both primary and secondary treatment facilities has been completed and the construction contract will be awarded in the fall of this year.

Bids were opened recently for the multimedia filtration facility substructure and outfall contract. Work under this contract will include construction of the chlorine contact tanks together with an outfall conduit to carry chlorinated effluent to the Potomac River. The outfall portion of the

contract is to be completed by July 1975 to permit early operation of the new secondary facilities. The remaining portion of the contract is scheduled to be completed by January 1976.

Construction of the solids processing building structure is now completed. Bids have been taken for the sludge dewatering facility. The incineration facilities contract is being reviewed by EPA prior to being let for bids.

Design of the chemical building to house the bulk storage facilities for chemicals (ferric chloride, alum, and polymers) has been completed and the contract awarded last winter. The designs for the nitrification reactors, nitrification sedimentation basins, nitrification blower building, and the lime-handling facilities have been done. Construction of these will be completed by the fall of 1976.

Design of the denitrification reactors, nitrogen release tanks, and denitrification sedimentation basins has been completed. Funds for these contracts have not yet been appropriated. Design of the multimedia filter and control facilities was completed last summer. Funds for construction of this phase of the project have not yet been allotted. Instrumentation for the advanced waste treatment facilities is under design.

Treatment

D.C.'s sewage program requires that all combined sewage flows up to two times the dry weather flow receive complete treatment, and that the excess between two times and five times the dry weather flow receive primary treatment and disinfection. All flows from the sanitary portion of the sewer system are to receive complete treatment and will be kept separate from flows emanating from the combined portion of the sewer system.

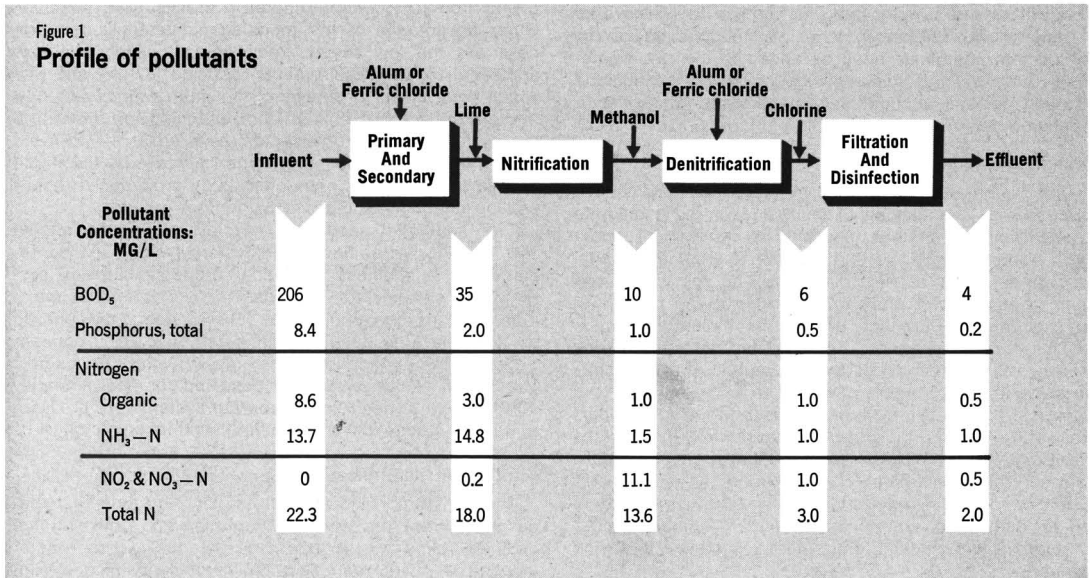
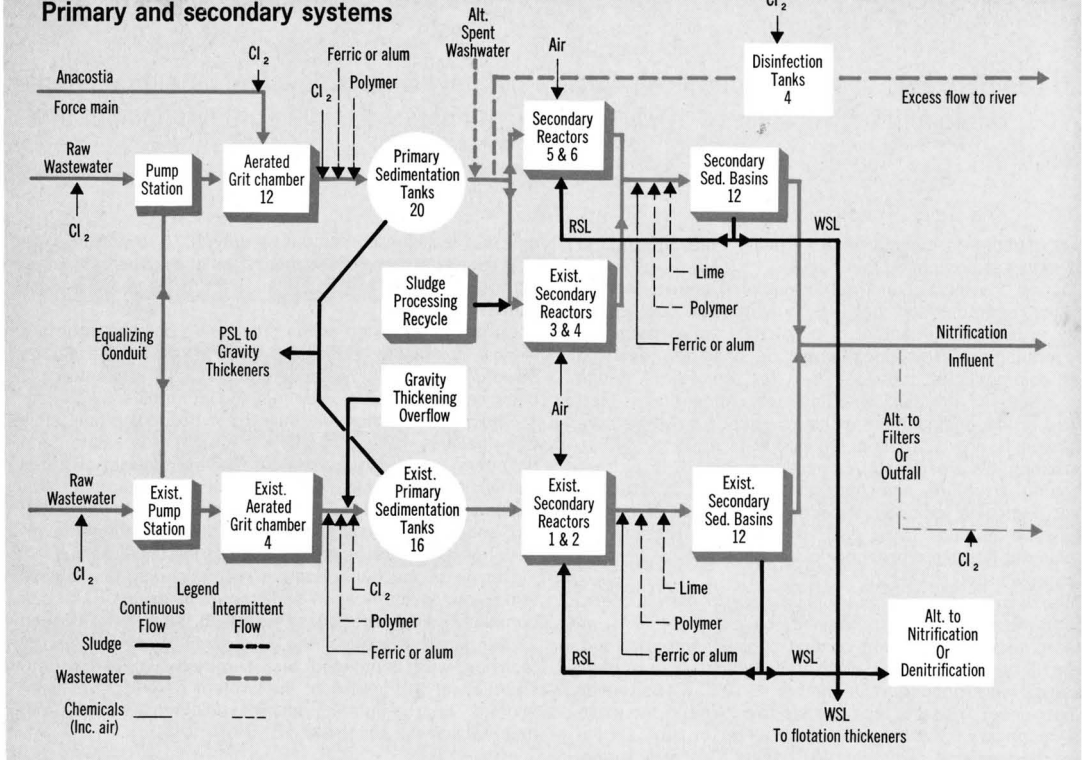


Figure 2

Primary and secondary systems



Primary treatment

Prior to the expansion program, raw wastewater was pumped to four aerated grit chambers and then discharged to 16 circular primary sedimentation tanks. These facilities had a maximum hydraulic capacity of approximately 300 mgd. Parallel new primary treatment facilities to handle the additional 350 mgd to receive complete treatment and the 289 mgd excess flow needing primary treatment have recently been completed. Dilute sludge from the primary tanks is pumped to six covered existing gravity thickening tanks. Although it is not expected that chemicals need be added to the raw wastewater, flexibility has been provided to allow the addition of a polymer and/or metal salt ahead of the primary sedimentation tanks.

Secondary treatment

This system will employ the modified activated sludge process with the addition of alum and/or ferric chloride to achieve a first-stage phosphorus removal of about 70%. Approximately two thirds of the total dose of metal salt will be added at this point. It will be possible to add alum to any reactor and ferric chloride to the remainder for experimental purposes, or if an insufficient supply exists for a single chemical. The modified activated sludge process effluent, enhanced by the addition of alum or ferric chloride, has proved to provide an excellent feed to a biological nitrification system. Because the process operates with very short sludge age, essentially no nitrates are produced, resulting in a more uniform ammonia concentration to the nitrification system and giving more satisfactory control of the nitrification reaction. In addition, the residual metal ions in the secondary effluent appear to improve the settling characteristics of the nitrifying sludge.

Operation of the EPA-DC pilot plant has indicated that 90% BOD removals are not required ahead of the nitrification process. However, it appears that the BOD concentration leaving the secondary system should be maintained below 50 mg/l. to ensure satisfactory nitrification. The modified activated sludge process with metal salt addition can consistently meet this requirement. From a cost standpoint, benefits of the increase in BOD removal efficiency from 75% without chemical to 85% with chemical. Other advantages of the modified activated sludge process are the low oxygen requirements which minimize additional blower requirements, and the low recycle rate which lends itself to obtaining maximum wastewater flow through the existing mixed liquor channels. In contrast to the sludge-bulking problems encountered at the EPA-DC pilot plant for other air and oxygen processes, the modified aeration process has consistently produced a rapidly settling sludge not subject to filamentous growths.

Two additional secondary reactors are being added. The existing spiral flow-air diffusion system will be replaced by a stainless steel coarse-bubble diffusion system. The system has been designed to meet the maximum 4-hr oxygen demand at MLVSS concentrations up to 1200 mg/l. to ensure a sufficiently low BOD concentration to the nitrification system during winter conditions. The return sludge system is designed for approximately 10% recycle at peak flow. Separate systems are provided to transfer sludge and scum to flotation thickening tanks.

Nitrification/denitrification

The nitrification system will employ plug-flow suspended growth reactors with sedimentation and return sludge facilities. Lime will be added to the nitrification reactor influent to offset reductions in alkalinity caused by up-

though chlorine can be added either before or after the filters, it is anticipated that continuous chlorine dosing ahead of the filters will be necessary to minimize backwash frequency and to reduce unsightly growths in the filter distribution channels. The filters will be uncovered, located on opposite sides of a central covered gallery.

Studies have been conducted at the pilot plant to evaluate various combinations of dual- and trimedia for the filters. The objective of this program was to develop a combination of media which will not require backwashing more frequently than every 12 hr at the 650 mgd peak flow without upstream addition of polymer. Results to date indicate that these criteria can be met by appropriate media selection but that there may be times when the nature of the biological floc will permit only a 6-hr run at peak flow. Consequently, the filter backwash system has been modified to permit a 6-hr backwash interval. If necessary, anionic polymer can be added to the denitrification system to produce an effluent of high quality to permit long filter runs.

Filter backwash will be equalized in large conduits located under the filter building prior to return upstream. Flexibility has been provided to return backwash either to the nitrogen release tanks or upstream of the secondary reactors. Normally, the return will be to the nitrogen release tanks. The filtered effluent is collected in two large conduits located between pairs of chlorine contact tanks. Space for future installation of mechanical mixers for chlorine diffusion has been provided in these channels. The disinfected plant effluent will be discharged to the Potomac River.

Sludge processing

Extensive studies have been completed to determine design data for flotation thickening, vacuum filtration, and incineration. These studies have shown that the chemical and biological sludges from secondary and advanced treatment thicken and dewater at least as well as pure biological sludges from conventional activated sludge systems. The sludge processing building will contain essentially all of the sludge processing components with the exception of the gravity thickening and sludge storage tanks.

Other design feature

The advanced wastewater treatment facilities are designed to be operated in two halves to permit comparative tests while operating at different MLSS concentrations, chemical dosages, and other variables. Satellite operating laboratories will be provided at key locations in

each treatment system to furnish up-to-the-minute analyses for process control.

As soon as the new sludge processing facilities become available, the existing digestion and elutriation processes can be abandoned. The space occupied by these facilities has been reserved for further treatment should wastewater reuse become a reality. The existing inactive sludge drying and incineration building is being converted to chemical storage facilities.

Process instrumentation

The treatment plant, when completed, will contain four computer systems, three for process control and one for data processing. One process computer will control the advanced waste treatment system. The other two are for primary and secondary treatment, and for solids processing.

The processes that will initially operate with these controls are return sludge, waste sludge, chemical treatment (lime, ferric chloride or alum, methanol, and polymer), and pumping.

All process data, equipment status, and alarms will be transmitted to the computers located in Satellite Operations Center (SOC), either as hard-wired electronic signals or multiplexed digital signals from remote data terminals, depending on the number and distance of signal sources to and from the computer center. As new, more precise, and reliable sensors become available, they can be accommodated within the proposed system as can new software control algorithms relating to process.

The influent flow to the secondary reactors will be metered by sonic flow measuring systems and controlled by computer. This system will also be used for pacing the alum or ferric chloride feed systems. The return sludge flow system to the secondary reactors will be provided with a flow regulating system to meter and control the return sludge flow to each reactor. The controls are arranged so that the output from the flow rate controller for any reactor becomes the set point, via ratio units, for the flow controller for the other reactors. A flow-regulating system will also be provided to meter and control the waste sludge flow.

The influent flow to the secondary reactors will be provided with a flow-regulating system to meter and control the return sludge flow to each reactor. The controls are arranged so that the output from the flow rate controller for any reactor becomes the set point, via ratio units for the flow controller for the other reactors. A flow-regulating system will also be provided to meter and control the waste sludge flow.

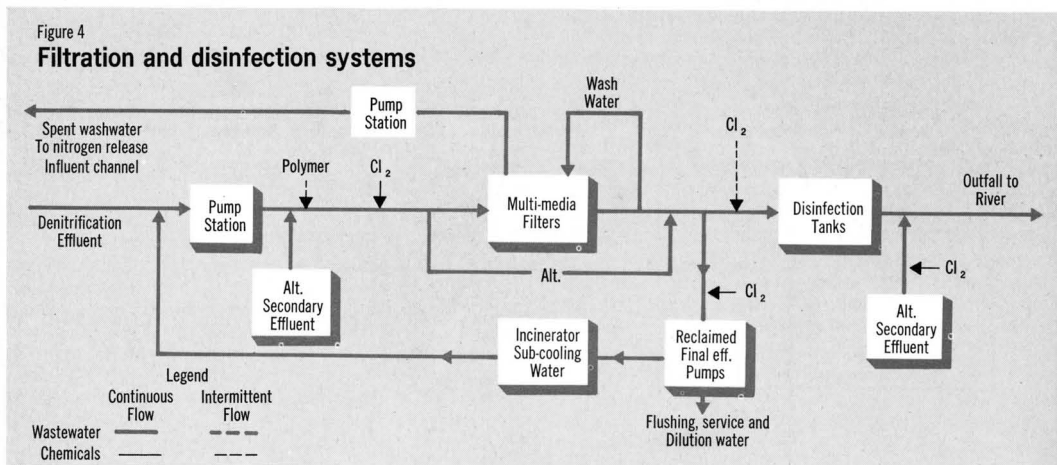
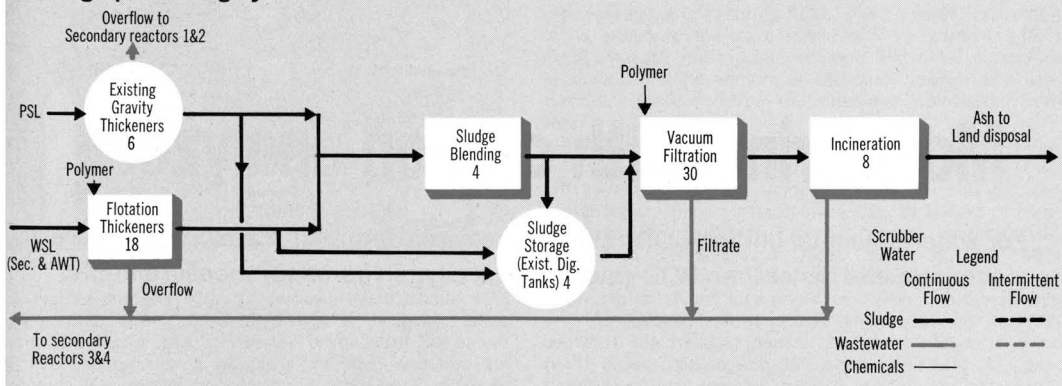


Figure 5

Sludge processing system



The influent flow to the secondary reactors will be continuously monitored for phosphate concentration by orthophosphate analyzers. Reactor-dissolved oxygen concentrations will be monitored by each reactor. Mixed liquor will be monitored for pH.

Chemical feed pumps for alum or ferric chloride will be controlled by "mass flow" or "pace and trim." "Mass flow" will be the product of secondary influent flow and phosphate concentration and will control pump speed only. "Pacing" will be by influent flow to each reactor to control pump speed, and "trimming" will be by phosphate concentration to control pump stroke. The pump-pacing control system will include a controller with an integral automatic-manual station, and with remote computer set point capability.

For advanced wastewater treatment, a pH monitoring and control system will be provided on the influent flow to the nitrification reactors. The signal will be utilized to trim the lime feed pumps to automatically control the pH. Ammonia and phosphorus analyzers will also be used to monitor the nitrification influent. Mixed liquor SS analyzers will be provided in the first stage of each nitrification reactor. Dissolved oxygen probes will be provided for the nitrification reactors to provide a complete oxygen profile.

Two return sludge flow-splitting systems containing six control loops will be provided on the return sludge flow from the nitrification sedimentation basins to the nitrification reactors. Each of the 12 return sludge flow control loops will consist of a rate of flow controller, flow transmitter, and flow indicating controller with remote set point adjustment. A rate of flow metering and control station is provided on the discharge of each of the 42 return sludge pumps. The pump discharge rate will be controlled by manual computer set point control of variable-speed drives on the pumps.

Dissolved oxygen analyzers and pH monitoring systems will be provided on the influent flow to the nitrification sedimentation basins. Each sedimentation basin will be equipped with sludge blanket level monitors for high- and low-level indication. Two waste sludge metering and control system will be provided on the discharge of the four waste sludge pumps. Each waste sludge metering and control system will meter and control the discharge from either of two waste sludge pumps.

Mixed liquor SS analyzers will be provided in the first stage of each denitrification reactor. A methanol feed pump control system will be provided for pacing of the six methanol pumps in direct relation to the influent flow and nitrate concentration. Ammonia-nitrogen, nitrate-nitrogen, dissolved oxygen, and phosphorus analyzers will be provided for the denitrification reactor influent chan-

nels. The denitrification sludge recycle and wasting systems and their instrumentation and control are similar to that employed in the nitrification system. Ammonia-nitrogen, nitrate-nitrogen, and phosphorus analyzers will be provided to monitor denitrification effluent.

A control center will be provided atop the multimedia filtration gallery from which all filters can be controlled. Rather than provide filter consoles at each filter, a communication system has been provided which will permit an operator to monitor backwashing of a filter by relaying directions to the control center. The filter control system will permit automatic sequential backwashing of the filters on the basis of head loss or alternatively at predetermined intervals. A turbidity monitoring system will also be provided for further protection against isolated breakthroughs. SS analyzers will be installed to monitor the filter influent. The filtered effluent will be continuously monitored for pH, dissolved oxygen, ammonia-nitrogen, nitrate-nitrogen, phosphorus, and chlorine residual.

When completed, the District of Columbia plant will be the largest advanced wastewater treatment plant in the world. Concurrent design and pilot plant testing have not only saved nearly two years' time but have also resulted in a design which contains a maximum of features proved to be desirable as a result of the testing program. The total project represents a remarkable political, environmental, and technical achievement to clean up a prized water resource.

Donald E. Schwinn is partner of Stearns & Wheeler, civil and sanitary engineers, Cazenovia, N. Y. Mr. Schwinn was formerly vice-president and chief, wastewater process engineering of Metcalf & Eddy. In that position, he was responsible for the pilot plant studies, alternate process evaluations, and process design of the District of Columbia's advanced waste treatment system.



George K. Tozer is vice-president of Metcalf & Eddy. Mr. Tozer has more than 20 years' experience in water pollution control engineering. In the past five years, he has served as project manager for many projects including the 60-mgd secondary treatment plant at Hartford, Conn., as well as the District of Columbia plant.



Coordinated by LCG

Monitoring with carbon analyzers

For water effluents, on-line COD (chemical oxygen demand) measurements are accurate and faster than BOD (biochemical oxygen demand) measurements

M. Louis Arin

Ionic, Inc., Watertown, Mass. 02172

Unquestionably, the first water pollution monitoring devices were man's senses of sight, smell, and taste. If the water looked, smelled, or tasted bad, the water was not consumed. However, a more objective measurement of the purity of water was needed if pollution control or the results of pollution control were to be measured.

BOD/COD

One measure of the polluting nature of a material is the determination of the amount of dissolved oxygen that will be consumed by microorganisms in the process of oxidizing the material to a stable form under aerobic conditions. This phenomenon is called biochemical oxygen demand—the robbing of dissolved oxygen from the marine life to oxidize the material.

The biochemical oxygen demand (BOD) of an effluent is an important property that should be monitored before allowing it to enter the ecosystem of a river or ocean. Such a criterion for water purity was first established by the English Royal Commission on Sewage Disposal in the late 1800's. The test involved placing a sample of diluted wastewater in a constant temperature environment and measuring the oxygen content of the sample over a period of time. Initially, a 20-day period was selected. The time period was eventually shortened to a minimum of 5 days to allow for the proper control of a sewage treatment plant.

BOD measurements not only suffer from lengthy minimum time but from other limitations:

- separation of insoluble inorganics (fats, oils, hydrocarbons) from the liquid phase that cause low BOD values
- oxidation of inorganics, such as ferrous iron, sulfide, and sulfite, that cause BOD values
- presence of toxic materials that cause low BOD values unless properly adapted by a seed organism
- presence of lignin (major contaminant of wood pulping wastes) that causes low BOD values.

Because of these considerations and a reproducibility of only $\pm 20\%$, other on-line pollution monitoring methods were sought.

The chemical oxygen demand (COD) measurement was the next stage in the search for a more rapid and accurate measurement of the level of water pollution. A powerful oxidizing agent, such as potassium dichromate, is substituted for the bacteria which carry out the oxidation in the BOD determination. In the COD determination, the amount of CO_2 evolved or, more conveniently, the

amount of dichromate reacted is measured. Because of the more severe oxidizing conditions of the COD determination, the results of COD tests are usually higher than those of the BOD tests. Some organic materials completely oxidized in the COD test are only slowly decomposed by the microorganisms in the BOD test.

Like the BOD analysis, COD measurement has limitations including:

- length of test period— $\frac{1}{2}$ –3 hr
- slow oxidation of pollutants, such as pyridine, benzene, ammonia, and acetic acid, leading to low results
- inapplicability of the method to straight chain and aromatic hydrocarbon wastes, such as n-hexane and n-heptane, that remain on surfaces and yield low results
- presence of chlorides that produce high results unless complexed by the addition of mercuric sulfate to the sample before refluxing
- special handling required of hazardous chemicals
- reproducibility of $\pm 8\%$.

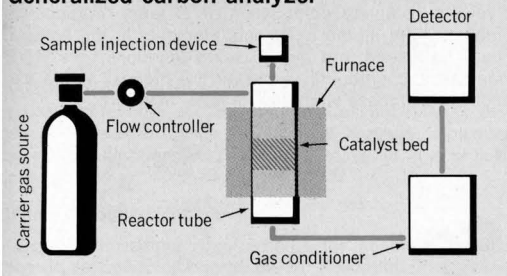
Many laboratory techniques for measuring the carbon content of water samples have been developed (Hill, H. N., "Carbon Analysis," 23rd Annual ISA Conf., New York, N.Y., October 28, 1968). It was not until the early 1960's that Van Hall (Van Hall, C. E., et al., *Anal. Chem.*, **35**, 315, 1963) at Dow Chemical and workers at Union Carbide reported the development of simple rapid combustion methods for the determination of organic substances in aqueous solution. These workers initiated a new generation of pollution monitoring instruments capable of real-time pollution monitoring.

Carbon measurements

By definition, the most general characteristic of the organic compounds is the presence of carbon atoms in their structures. Consequently, carbon analyzers have been used extensively for the nonspecific detection of organic compounds in water samples. The common carbon oxidation reaction is $[\text{C}] + [\text{O}] \rightarrow [\text{Ox Prod}]$, where $[\text{C}]$ represents the carbon atoms in the organic compound to be measured; $[\text{O}]$ represents an oxidizing compound (oxygen, chromate, water); $[\text{Ox Prod}]$ represents products of the oxidation reaction (carbon dioxide, carbon monoxide). The range of oxidizing temperatures may vary from near room temperatures for biological oxidation to 1000°C in a catalytic furnace. In the pollution monitoring carbon analyzers, a catalytic furnace is used so that the oxidative process may be performed in minutes instead of days.

Figure 1

Generalized carbon analyzer



A typical analysis (Fig. 1) involves the injection of a sample onto the catalyst bed where oxidation takes place. The carrier gas carries the products of the oxidation reaction through a sample conditioner and into the detector. The analytical instruments, however, differ in design and with regard to the nature of the component monitored.

A total carbon (TC) analysis measures the sum of organic and inorganic carbon present in a water sample. A sample is injected onto an oxidizing catalyst bed and the carbon dioxide generated from the carbon present in the sample is measured. Although this method has the advantage of being a sensitive simple measurement, it does not distinguish between organic and inorganic carbon. The TC analyzer manufactured by Ionics, Inc., oxidizes organic compounds via the reforming reaction of water on a fixed bed of palladium metal at 950°C, whereas Enviro Control, Inc., carries out the oxidation reaction of water on a fluidized bed of aluminum oxide in air at about 900°C. Another manufacturer, Astro Ecology, Inc., has a fixed bed reactor composed of nonprecious metal materials at about 900°C.

A total organic carbon (TOC) analysis measures the difference between TC and total inorganic carbon (TIC). If we assume that the major inorganic carbon contribution is due to the presence of carbonate, there are two procedures for measuring TOC. One common procedure is to eliminate the carbonate from the sample before measuring its total carbon content. The other procedure is to measure the amount of carbonate present and subtract its contribution from the measured total carbon content.

Methods used to eliminate carbonate ion from water solutions include the precipitation of carbonate with barium hydroxide and the acidification of the solution, followed by expulsion of the evolved CO₂ by boiling or purging with inert gas. Van Hall & Stenger's method (Van Hall, C. E., Stenger, V. A., *Anal. Chem.*, **39**, 503, 1967) for the direct determination of carbonate consists of introducing a 10–50 µl sample containing carbonate ion onto a catalyst bed at 150°C and measuring the CO₂ evolved. The catalyst bed is composed of quartz chips (6–12 mesh) coated with 85% phosphoric acid. A similar direct analytical method using a catalytically active salt has been developed by Arin at Ionics, Inc. Astro Ecology, Inc., Delta Scientific, and Ionics, Inc., have developed the acidification and purge technique. Though reliable, it suffers from the disadvantage of eliminating volatile hydrocarbons from the sample during the purge step. To circumvent this difficulty, Ionics, Inc., has developed a TOC analyzer utilizing the direct determination of carbonate method.

The two most common detectors used in total carbon analyzers are the nondispersive infrared (NDIR) analyzer sensitized to carbon dioxide and the flame ionization detector (FID). Van Hall, in studying possible interferences with the total carbon measurement using an infrared analyzer, found substantially no interferences except for a slight interference from strong brines and certain acids. These solutions produced fogs that were counted as carbon dioxide by the infrared analyzer. The presence of a

Process analyzers

Instrument type	Manufacturer	Injection method	Catalysis method	Re- response time, min	Detector	Max concn range, ppm	Utilities, required
Total carbon/ total organic carbon	Astro Ecology Corp. (Houston, Tex.)	Sample metered, <100 µ particu- lates	Fixed bed, non- precious metal catalyst	10	NDIR	0–5000, carbon	Water, hydro- chloric acid
Total carbon/ total organic carbon	Delta Scientific Corp. (Linden- hurst, N.Y.)	Samples metered, <1000 µ particu- lates	Fixed bed, copper oxide, 900°C	5	Nephelometer	0–5000, carbon	Hydrochloric acid, barium hydroxide
Total carbon	Ionics, Inc. (Watertown, Mass.)	Slide plate valve, solids capacity: <200 µ particu- lates	Palladium, 950°C	5	NDIR	0–3000, carbon	Air, nitrogen
Total carbon/ total organic carbon	Ionics, Inc. (Watertown, Mass.)	Slide plate valves, <200 µ particu- lates	Total carbon: fixed bed, Pd catalyst, 900°C Inorganic carbon: acid salt catal- yst, 170°C	5	FID	0–5000, carbon	Air, hydrogen, nitrogen
Total carbon/ total organic carbon	Ionics, Inc. (Watertown, Mass.)	Slide plate valves, <200 µ particu- lates	Total carbon: fixed bed, Pd catalyst, 900°C Inorganic carbon: carbonate re- moved	5	NDIR	0–3000, carbon	Hydrochloric acid, air, nitrogen
Total oxygen demand	Astro Ecology, Corp. (Houston, Tex.)	Sample metered, <100 µ particu- lates	Fixed bed, non- precious metal catalysis, 900°C	10	Zirconium oxide detector	0–20,000, TOD	Water
Total oxygen demand	Enviro Control Inc. (Washing- ton, D.C.)	Sample metered, <100 µ particu- lates	Fluidized bed of Al ₂ O ₃ , 900°C	8	Polarographic- type sensor	0–4000, TOD	Air, water
Total oxygen demand	Ionics, Inc. (Watertown, Mass.)	Dow-Ionics rotary sampling valve, <200 µ particu- lates	Fixed bed, Pt, 900°C	3	Zirconium oxide detector	0–10,000 TOD	Nitrogen

FID: flame ionization detector; NDIR: nondispersive infrared analyzer.

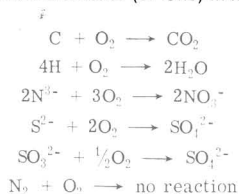
fine filter in the line to the infrared analyzer minimized this interference by removing most of the particulate matter. The flame ionization detector has a wide dynamic response range but requires a catalyst to convert the CO₂ to methane. Methanizer catalysts can be susceptible to poisoning from sulfur-containing compounds.

The detector system used in the analyzer developed by Delta Scientific Corp. quantitatively measures the barium carbonate precipitate formed when carbon dioxide reacts with a barium hydroxide solution. The increase in turbidity caused by the precipitate formation is proportional to the amount of carbonate in the sample.

Of all the automated analytical methods, the total oxygen demand measurement (TOD) is probably closest in concept to the original concept of the BOD measurement. In the BOD measurement, one measures the uptake of dissolved oxygen by microorganisms over a period of 5–20 days. In a similar manner, the TOD analysis measures the rapid uptake of oxygen due to the catalytic oxidation of oxidizable material on a catalytic bed at 900°C. But unlike the BOD test, many compounds in the TOD test are rapidly oxidized at 900°C, compounds that would only be slowly attacked by microorganisms near room temperature.

In a TOD analyzer, a sample is injected into the reaction tube where the oxidizable sample components undergo rapid catalytic oxidation. This reaction temporarily disturbs the oxygen equilibrium resulting in a momentary oxygen depletion in the continuously flowing carrier gas.

The depletion is accurately measured and is directly related to the oxygen demand of the sample. Ideally, to measure the oxygen demand accurately, it is desired to achieve a complete combustion or at least reproducible combustion for all the oxidizable elements in the sample. Thus it is desired that the following reactions take place since the end products represent the highest stable oxidation state of these elements (or ions) in nature:



Clifford (Clifford, D. A., "Automatic Measurement of TOD," 23rd Annual Purdue International Waste Conf., Purdue University, Lafayette, Ind., May 9, 1968) examined the temperature interval between 500–1000°C for optimum operation and found that the peak heights did not increase significantly above 900°C or improve upon the precision of the measurement. Complete combustion was found for compounds containing carbon, hydrogen, oxygen, nitrogen, and salts of organic compounds. The compounds examined were sodium acetate, sucrose, potassium acid phthalate, phenol, benzoic acid, ethanol,

Laboratory analyzers

Instrument type	Manufacturer	Injection method	Catalysis method	Response time, min	Detector	Max concn range, ppm	Utilities required
Total oxygen demand	Astro Ecology Corp. (Houston, Tex.)	Metered into system	Fixed bed, non-precious metal catalyst, 900°C	10	Zirconium oxide detector	0–30,000, TOD	Water
Total organic carbon/total carbon	Astro Ecology Corp.	Metered into system	Fixed bed, non-precious metal catalyst, 900°C	10	NDIR	0–15,000, carbon	Water
Total organic carbon/total carbon	Beckman Instruments (Fullerton, Calif.)	Syringe	Total carbon: cobalt oxide, 900°C Inorganic carbon: phosphoric acid on quartz	2–4, 150°C	NDIR	0–4000, carbon	Air or oxygen
Total organic carbon	Carle Instruments Inc. (Fullerton, Calif.)	Syringe	Volatilization into FID	20	FID	Function of volatilization time	Nitrogen, hydrogen
Total organic carbon/total carbon	Dohrmann Div., Envirotech Corp. (Mount View, Calif.)	Syringe	Cobalt oxide, 900°C	5	FID	0–1999, carbon	Hydrogen, air, nitrogen, water
Total organic carbon/total carbon	Enviro Control (Rockville, Md.)	Metered into system	Fixed bed, copper oxide, 920°C	4½	FID	0–1000, carbon	Hydrogen, air, nitrogen
Total organic carbon/total carbon	Ionics, Inc. (Watertown, Mass.)	Syringe	Total carbon: palladium, 900°C Inorganic carbon: acid salt, 170°C	2–4	NDIR	0–2000, carbon	Nitrogen
Total organic carbon/total carbon	Oceanography International (College Station, Tex.)	Ampul, 10 ml	Sample heated in ampul with oxidizing agent	2–5	NDIR	—	Oxygen, propane, nitrogen
Total oxygen demand	Astro Ecology Corp. (Houston, Tex.)	Metered into system	Fixed bed, non-precious metal catalyst, 900°C	10	Zirconium oxide detector	0–30,000, TOD	Water
Total oxygen demand	Ionics, Inc. (Watertown, Mass.)	Slide valve	Platinum, 900°C	3	Platinum-lead fuel cell	1000, TOD	Nitrogen, air
CO ₂ D method	Precision Scientific (Chicago, Ill.)	Syringe	Fixed bed, platinum, 900°C	2	NDIR (carbon monoxide sensitized)	300, COD COD	Carbon dioxide

pyridine, cyanide, and urea. Sodium sulfites and sulfides were not fully oxidized to their highest oxidation states. Clifford found them to be approximately 75% oxidized.

As TOD analysis monitors the depletion of the oxygen level in a carrier gas, any compound (nitrates) that releases oxygen upon heating would interfere with the measurement. At Ionics, it has been found that in neutral or basic solutions, sodium sulfate does not release oxygen in agreement with the Clifford findings. However, there are indications that oxygen is released in acid solutions.

On-line pollution monitors

One of the prime requirements for an on-line instrument is reliability of operation. In the optimum situation, an instrument should be capable of being left to function independently for at least one week. It is this requirement that distinguishes the laboratory unit from the process instrument.

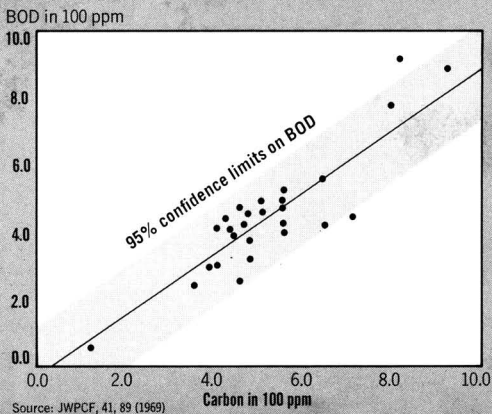
The part of the carbon analyzer requiring the greatest amount of attention is the sample injection system. The most difficult step in any analysis is to introduce a known amount of sample accurately and reliably into the analytical system. The laboratory model carbon analyzers use the technique of syringing either through a septum into the catalytic oxidizing furnace or into a ceramic boat subsequently placed into a catalytic oxidizing furnace. The process analyzers currently on the market generally use either one of two modes of sample injection, namely, the automatic sample injection valve or the slow metering of the sample into the system.

The basic operation of the automatic sampling valve involves trapping a small sample (20–40 μ l) in a hole with a precision bore and forcing it into the catalytic oxidation furnace. The slider, actuated (pushed back and forth) by air pressure, is usually constructed of glass-filled Teflon, Rulon, or some similar type of self-lubricating material. The carrier gas is used to force the water sample out of the compartment onto the catalyst bed. Ionics, Inc., uses this type of valve in their TC and TOC analyzers.

A different approach to the injection of discrete sample was developed at Dow Chemical and licensed to Ionics, Inc. In the Dow-Ionics rotary sampling valve, a syringe is mounted inside a rotating aluminum head that rotates around the center post over a trough containing a flowing sample. The plunger is raised slowly to aspirate a 20- μ l sample from the trough into the syringe. When the head rotation brings the syringe over the injection hole above the catalyst bed, the sample is injected. This valve avoids the necessity for air actuation of the sampling valve. Ionics reports that both the slide injection valve and the rotary sampling valve are capable of handling samples containing particles up to 200 μ in diameter.

Figure 2

Correlation curve of total carbon and BOD



A technique involving the continuous metering of sample into the catalytic oxidation furnace is used by Astro Ecology, Delta Scientific, and Enviro Controls. The sample is metered into the reactor at flow rates between 0.5–4 ml/min. This technique was developed to increase the ability of the analyzer to handle samples containing suspended solids. Astro Ecology and Enviro Controls claim the ability to handle particles up to 100 μ in diameter. Delta Scientific specifies a maximum particle size of 1000 μ in diameter. Currently, there are no objective data on the capabilities of the different techniques.

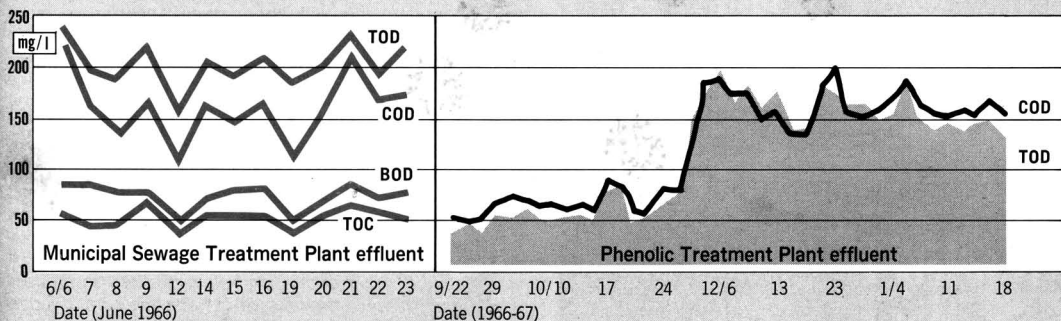
Correlations and applications

A large number of experiments were performed to examine the correlation between BOD and COD measurements and the more recent rapid carbon analysis methods. A correlation between BOD and TOC of an effluent from a sulfite paper mill was reported by Ostendorf and Byrd (Fig. 2). Robbins, Kriz & Howells reported on the measurements of total organic carbon in swine waste effluents and on the correlation of TOC and BOD measurements. They found poor correlation between BOD and TOC, attributed to antibiotics and other additives which affect BOD results.

Correlation of TOD, COD, BOD, and TOC measurements were taken of the primary effluent from a sewage treatment plant in Midland, Mich. (Fig. 3). The TOD measurement is consistently greater than the COD but both follow the same trend. These samples contained suspended solids included in the determinations. The discrepancy between TOD and COD measurements was at-

Figure 3

Correlation of TOD, COD, BOD, TOC

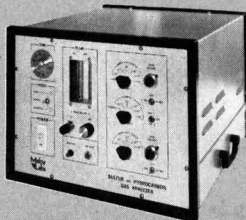


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tributed to the more efficient oxidation of the particulates in the TOD measurement. This was observed from experience with filtered and unfiltered samples. There were no comments, however, on why the TOC values were constantly lower than the BOD values. Correlation of TOD and COD at the Dow phenolic treatment plant effluent was also reported.

In addition to monitoring the effluents from waste treatment plants, automatic carbon analyzers may be used to monitor the efficiency of industrial processes. A West Virginia (Hill, H. N., "Carbon Analysis," 23rd Annual ISA Conf., New York, N.Y., October 28, 1968) chemical plant installed a TC analyzer as part of its monitoring system. During a three-day weekend, while supervisory and maintenance personnel were working only skeleton crews, a waste treatment plant operator noticed a very gradual increase in the total carbon analysis data from one of the process sewers. This slow but definite increase was carefully watched until a production operator who was more familiar with the process equipment came on the shift. The production operator checked the side temperature controller on one of the large distillation columns and it was found to be inoperative and the temperature was dropping slowly. The estimated savings derived from fixing the temperature controller more than paid for the complete TC analyzer installation, including the telemetry equipment.

Okseter & Aschliman reported the use of a TOD analyzer together with a gas chromatograph to monitor pollution levels and to identify sources of pollution at the Humble Refinery (Baytown, Tex.). The TOD/GC instrumental combination monitored a daily wastewater volume of 20 million gal. The wastewater was first passed through an oil-water separator, then to a secondary treatment system which consisted of an eight-acre aerated lagoon, followed by a series of three natural lagoons. The TOD/GC pollution monitoring system was located between the oil-water separator and the secondary treatment system. The BOD and COD tests were not used for this application because they were time consuming and did not identify the components causing the pollution.

On one occasion, an increase in TOD readings was caused by methyl ethyl ketone (MEK) and diethylene glycol (DEG). Both components were traced back to their sources and stopped the same afternoon. The MEK originated at the MEK dewaxing unit and DEG was traced to a leaking safety valve at the benzene extraction unit. Another incident revealed that there was an excessive amount of sulfolane in the waste stream due to a leaking pump gland where sulfolane was coming in contact with cooling water. This loss would have cost \$3000 a day if it had not been detected. The pollution load to the wastewater treatment facility was reduced 25-30% the first year.

Because of its nonspecificity, the carbon analysis offers a general tool for monitoring municipal and industrial effluents and for industrial process control. Once a change is detected with the carbon analyzer, a more specific analytical instrument may be applied to ascertain the specific cause of the change. The TC, TOC, and TOD analyzers offer a rapid means of monitoring effluents and industrial processes but one must be aware of their limitations if the analyzer is to be applied successfully.



M. Louis Arin is a senior chemist with the instrument division at Ionics, Inc. He has been involved with the design and construction of the process total oxygen demand analyzer, development of catalysts for a process organic carbon analyzer, and other instrumentation.

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CIRCLE 11 ON READER SERVICE CARD

Complying with discharge regulations

Spokesmen of the federal Environmental Protection Agency spell out how industries and municipalities must keep tabs on their wastewaters, and how they can get help in the task of achieving compliance

Carl J. Schafer and Nicholas Lailas
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Washington, D.C. 20460*

The Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500), transformed the basis of enforcement activities concerning water pollution by eliminating the traditional enforcement conference, and replacing the 180-day notice procedure with an administrative permit procedure and provision for prompt court action against violators.

In enacting the new legislation, Congress stated that the national goal is to eliminate the discharge of pollutants into navigable waters by 1985. An interim goal, where attainable, is to achieve, by July 1, 1983, water quality sufficient for the protection and propagation of fish and shellfish, and for recreation in and on the water. In order that such goals be reached, the Act requires establishment of effluent limitations based on "best practicable control technology currently available" (BPCTCA) by July 1, 1977, and "best available treatment economically achievable" (BATEA) by July 1, 1983. These effluent limits apply to point sources discharging to navigable waters.

Discharge permits

P.L. 92-500 defines "point source" as "discernible, confined, conveyances" which encompass any pipe, ditch, channel, tunnel, conduit, discrete fissure, container, rolling stock, vessel, or cattle feedlot. The Act defines "navigable waters" as "waters of the United States." This has been interpreted to include all interstate waters, all navigable waters, and any interstate nonnavigable river, stream, or lake utilized by industries in interstate commerce, or used by interstate travelers for recreational or other purposes. Actually, this latter definition applies to virtually all surface waters of the United States.

A major facet of this law is the establishment of a new national permit system called the National Pollutant Discharge Elimination System (NPDES). Under this program, industrial, municipal, and other point source dischargers must obtain permits setting forth specific limitations on the discharge of pollutants into the navigable waters of the United States.

The staggering task of issuing 40,000 permits regulat-

ing the discharge of pollutants to the nation's waters is well under way toward meeting the objectives set under P.L. 92-500. By December 31, 1974, EPA and the states will have issued 2800 permits to major industrial dischargers, controlling approximately 80% of the total pollutants discharged by industry. The issuance of the remainder of industrial permits, aimed at covering all of the industrial dischargers, will be completed by July 1, 1975.

The program is administered by officials in each of EPA's 10 regional offices, and coordinated nationally by the EPA's Permit Assistance and Evaluation Division, headed by Acting Director, Robert B. Schaffer.

As of July 1, 1974, some 8000 industrial permits (including both major and minor dischargers), out of about 28,000, have been issued. In addition, some 4000 municipal permits, out of a total of about 16,000, and almost 1000 permits for state and federal facilities (military bases, state hospitals, schools); and about 200 agricultural permits, mostly for feedlots, were issued.

An important aspect of the program to regulate the discharge of pollutants to the waters of the United States is the emphasis on state participation. As this goes to press, authority to administer and enforce the regulations has been delegated to 15 states, with 10 more expected to join the program by December 31, 1974. States that will achieve this status later are being encouraged to take over as much of the necessary activities as possible. EPA is cooperating fully with the states in decentralizing the authority and enforcement requirements that are vital to protecting the nation's waters.

Permit provisions

The permit to be issued under the NPDES will have a basic format of effluent limits, a compliance schedule, and monitoring requirements. The 1977 and 1983 dates are targets to be viewed as the outside limits for compliance. The Act envisions that to meet effluent limitations, there will be stages of compliance described as the attainment of levels of substantial improvement even before these legislative dates.

The compliance schedule may contain dates for achieving certain levels of progress such as preparation of engineering reports, final construction plans, beginning and completion of construction, and, finally, operation of facilities. Interim dates and requirements are specified in the permit as a means of monitoring progress and minimizing slippage. For each interim date, the permittee must submit a written notice of compliance or noncompliance with the interim requirements. Where such interim dates may not be appropriate, reports of progress will be required at least every nine months.

Typical self-monitoring parameters

Industry	BOD	COD	Metals	TSS	Oil	pH	Flow
Food products	×			×		×	×
Forest products	×			×		×	×
Chemicals	×	×		×	×	×	×
Metal processing			×	×	×	×	×
Mining			×	×		×	×

The permit may therefore have more than one set of effluent limits. These limits are to be attained on dates conforming with the compliance schedule. The limits will be stated in quantitative terms such as kg (and lb) per day, except where this is not relevant, as in the case of pH or temperature, for example. Limitations may be expressed as concentrations in instances in which the rate of pollutant generation is not directly linked to the production effort, such as in mining, or where other requirements, such as removal of toxicity, apply. The effluent limits would be defined in terms of average and maximum kg (or lb) per day. These limits are based on effluent limitations or water quality standards, whichever is more stringent. For example, the pH limit is in the range of 6–9 unless water quality of the receiving stream requires some variation.

Effluent guidelines

P.L. 92-500 charges the EPA administrator with the task of publishing regulations providing "guidelines" for uniform effluent limitations for point sources from industrial categories. These effluent limitations, reflected in the permits, are the ones which shall require the application of BPCTCA for the 1977 target date and BATEA for the 1983 target date. Three major points are identified in the regulations.

First, the regulations will give meaning to the terms "best practicable" and "best available" when applied to various categories of industries. To define "best practicable" and "best available" for a particular category, such factors as the age of the equipment and facilities involved, the process employed, the engineering aspects of the application of control techniques, process changes, and nonwater quality environmental impact (including energy requirements) are taken into account. To assess "best practicable control," a balancing test between total cost and effluent reduction benefits is made. "Best available" technology is the highest degree of technology that has been demonstrated as capable of being designed for plant scale operation; thus, economic feasibility is a factor in interpreting "best available" treatment.

Second, with "best practicable" and "best available" having been interpreted, guidelines were published to establish "effluent limitations" to be imposed on classes and categories of dischargers. In these guidelines, the degree of pollution abatement attainable through the application of the "best practicable control" and "best available technology" in terms of amounts of constituents and chemical, physical, and biological characteristics of pollutants are identified. These guidelines can then be applied in setting specific effluent limitations in NPDES permits regulating individual point source discharges.

Third, the regulations identify control measures and practices to eliminate the discharge of pollutants.

To date, such effluent limitation guidelines have been promulgated for 30 industries, including almost 200 separate subcategories.

Meeting standards

The new Act includes the concept of water quality standards to be achieved in 1977 and 1983. Water quality standards, adopted and enforced by the original Federal Water Pollution Control Administration (FWPCA) for interstate waters, are continued in effect and can be updated, and new ones are to be established for intrastate water bodies where not previously adopted by the states.

If water quality cannot be protected by the application of best practicable control technology for industries and secondary treatment for municipal wastes before 1977, then effluent limitations for individual discharges will be set which will protect water quality standards. Before 1983, if best available treatment and its equivalent for municipal facilities do not contribute to attainment of water quality which will protect public water supplies, be adaptable to agricultural and industrial uses, protect a population of fish and wildlife, and allow recreational activities, more stringent effluent limitations will be imposed.

Permits are to be issued for fixed terms. The maximum duration of a permit will be five years (unless a new source is involved), and it is expected that the majority of permits will be written for the period since they will involve a commitment to a long-term abatement program.

It is to be noted that the new permit system applies only to those organizations that discharge their wastewaters directly into the waters of the United States. Such wastewaters include not only process wastewaters but sewage, utility wastewater such as boiler blowdown and water treatment waste, and cooling waters. Every discharge pipe must be included in a permit.

Manufacturing plants discharging to a municipal or publicly owned treatment works will be required to meet certain pretreatment requirements. In essence, these pretreatment requirements are established for the purpose of assuring that pollutants reaching the receiving waters will not be in excess of that limit which would be allowed if the discharge were direct.

Typical sampling and analysis frequency for self-monitoring parameters

Process effluent volume, mgd	Frequency (24-hr composites/week)
Less than 0.05	1 ^a
0.05-1.0	1
1-10	1-3
10 plus	3-5

^a May be reduced to 1 per month if the discharge does not contain toxic pollutants or affect the waters of another state.

Monitoring requirements

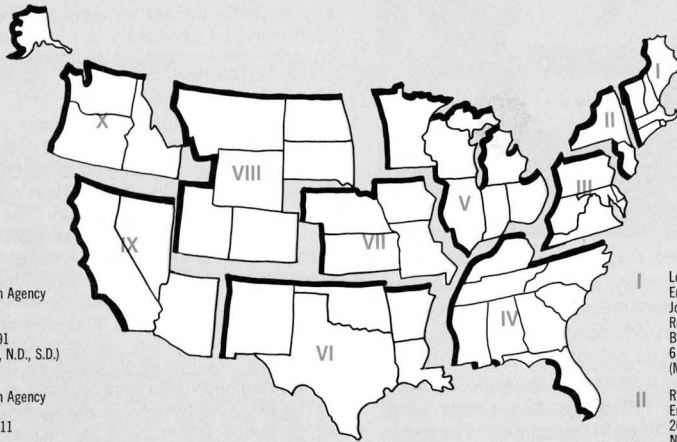
The self-monitoring requirements contained in the permit are developed on an individual basis, with consideration given to the type of treatment, the impact of the proposed treatment facility on the receiving waters and the parameters to be measured. The purpose of the monitoring program is to establish that the treatment facility is consistently meeting the effluent limitations imposed in the permit.

All permits must specify the following points:

- sample type
- frequency of analysis
- frequency of reporting to the regulatory agency.

For industry, EPA has described major parameters

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common to broad industrial categories. The 10 EPA regional offices or the individual states may add or delete parameters as required by water quality standards, or as necessary to conform to applicable effluent guidelines. Apart from industries' in-house monitoring and reporting requirements, there may be a few critical situations in the case of a substance, for example, whose discharger will be required to analyze the effect of his discharge on the receiving water.

Toxic pollutants are not listed because of the wide variety of these substances that industries can discharge. Effluent limitations for such pollutants are being established in accordance with Section 307 of P.L. 92-500. As these guidelines are promulgated, industry will be required to monitor and report on toxic substances so limited in specific discharges. However, uncontaminated cooling water discharges need not be monitored more frequently than reporting requirements call for, unless thermal or hydraulic conditions dictate otherwise.

When minimum sampling and analysis frequencies are being evaluated, the following considerations must be taken into account:

- **Compliance schedules**—The EPA suggests that monitoring requirements during construction stages of the compliance schedule, when abatement facilities actually are being built, be less than those during operation of the facilities.

- **Wastewater detention time**—Wastewater treatment facilities with short residence times are to be sampled more frequently than wastewater treatment facilities with long residence times. Residence times are decided on an individual basis according to the nature of the pollutant.

When determining monitoring and self-reporting requirements, the agency also will take into consideration the potential for failures of any given plant's abatement system. These considerations include receiving water quality, plant size, plant age, process technology employed, potential presence of toxic or hazardous materials, and engineering judgment as to the discharger's capability to fulfill his requirement.

Reporting discharges

The average monthly value reported for each type of analysis performed should be the average of all analyses of any given type actually performed, and not be limited to the minimum requirements specified in the permit.

The actual form upon which data will be recorded (EPA's "Monitoring Discharge Form" EPA-3320-1) registers minimum, average, and maximum values in terms of quantity and concentration as obtained from the analysis performed. The minimum and maximum values required are representative of a 24-hr day of actual manufacturing. In some situations the analytical value may be the result of a single composite analysis, while in others it may be the average of three 8-hr composite samples.

The form was developed to report self-monitoring data which dischargers must provide as specified in the permits. Prior to sending the forms to the permittee, the permit office enters such data as identifying information, specific parameters, effluent limits, and sampling and analyses requirements. The form may be used for the combined effluent measurements of an entire facility, combinations of selected outfalls, or a single outfall. The discharger will be required to file monitoring discharge

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CIRCLE 10 ON READER SERVICE CARD

reports with EPA regional offices or approved state of-fices on a regular basis.

In cases of noncompliance with the effluent limitations, the permittee must notify the EPA regional administrator or the director of the approved state agency. The permittee is required to take all reasonable steps to minimize any adverse impact to navigable waters, and increase monitoring as necessary to determine the nature and impact of the noncomplying discharge.

Monitoring seminars

The EPA is planning to present a series of Monitoring Industrial Wastewater Seminars this fiscal year. This seminar series is being sponsored by the Technology Transfer Program in cooperation with the Permit Assistance and Evaluation Division. The one-day seminar is structured to provide assistance for the manager of a medium-size plant who has overall responsibility for developing and implementing a sound monitoring program.

Technology Transfer held its first seminar for industry on Monitoring Industrial Wastewater in Atlanta this past April. The monitoring seminar, attended by 300 plant managers, featured a welcome address by John C. White, Region IV EPA deputy regional administrator.

The morning session of the seminar covered EPA regulatory policy with regard to the monitoring requirements of P.L. 92-500. Representatives from Florida, Kentucky, Georgia, Mississippi, North Carolina, South Carolina, and Tennessee discussed the states' relationship to the federal program.

The afternoon session offered technical guidance for implementing a monitoring program, presented by well-known and authoritative consultants in the field of wastewater treatment and monitoring. Topics presented included an overview of monitoring industrial wastewater, sampling, flow measurement, analytical quality control, and in-process monitoring.

Ten monitoring seminars (one for each regional office) are now being scheduled. The tentative schedule by region is as follows:

- October 1, 1974—Boston
- October 3, 1974—New York
- November 12, 1974—Atlanta
- November 14, 1974—Philadelphia
- November 26, 1974—Chicago
- December 10, 1974—Seattle
- December 12, 1974—San Francisco
- February 19, 1975—Kansas City
- February 21, 1975—Denver
- March 11, 1975—Dallas

Plant managers and others responsible for water pollution control interested in self-monitoring requirements and technology, should contact the appropriate Technology Transfer Regional Chairman (see map) for specific dates and locations of these seminars.



Carl J. Schafer is chief of the permits assistance branch of the EPA's Office of Water Enforcement. He is responsible for quality control, technical assistance, and policy coordination for EPA regions and states writing NPDES permits.



Nicholas Lailas is a physical science administrator in the EPA's Office of Technology Transfer. He has overall responsibility for developing a technology transfer program in monitoring and instrumentation, water supply, and the nonpoint source area.

Quenching of Singlet Molecular Oxygen by Some Atmospheric Pollutants

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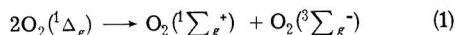
■ Room temperature rate constants for the deactivation of singlet molecular oxygen $O_2(^1\Delta_g)$ by SO_2 , H_2S , CH_3SH , CH_3COCH_3 , CH_2O , ambient air, and dry synthetic air were measured in a 220-m³ low-pressure reactor under static conditions. Emission at 7620 Å from $O_2(^1\Sigma_g^+)$, which is continuously produced from the energy pooling reaction $2O_2(^1\Delta_g) \rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-)$, was taken as a relative measure of the $O_2(^1\Delta_g)$ concentration in the system. The compounds deactivate singlet oxygen at rates comparable to or lower than ground state molecular oxygen. The rate constants for deactivation by CH_3SH , dry air, and ambient air are critically compared with literature values. It is concluded that singlet oxygen does not contribute to the atmospheric conversion of the trace gases investigated.

Since the role of singlet molecular oxygen $O_2(^1\Delta_g)$ in air pollution is still a matter of discussion (1), it is evident that more data on the physical and chemical quenching of this excited molecule by atmospheric gases and air pollutants are needed. We wish to report some $O_2(^1\Delta_g)$ quenching rate constants obtained from experiments in a 220-m³ stainless steel sphere. The reactor, as well as the experimental method, has been described in previous publications (2, 3). Briefly, $O_2(^1\Delta_g)$ was generated by passing a stream of high-purity oxygen (Air Liquide A 48) through a microwave discharge. The effluent gas was fed into the previously evacuated reactor up to a pressure of 7 torr. Atomic oxygen was eliminated by passing the discharged gas over a HgO film (4) and by reaction with 0.4 torr NO_2 which was introduced into the reactor before each experiment.

A quenching gas was subsequently added and the first order decay of $O_2(^1\Delta_g)$ in the reactor measured at various pressures. The decay can either be observed directly by measuring the infrared atmospheric band $O_2(^1\Delta_g \rightarrow ^3\Sigma_g^-)$ at 1.27 μ using a lead sulfide detector, or indirectly by measuring the intensity of the atmospheric band $O_2(^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-)$ at 7620 Å, which decays twice as fast as the infrared atmospheric band, with an infrared sensitive photomultiplier. Both methods have been used in this laboratory and found compatible (2, 3).

The second method was chosen in this work because of its higher sensitivity. The atmospheric band was isolated by a Schott interference filter centered at 7600 Å and the

intensity measured with a liquid nitrogen-cooled EMI 9558 B photomultiplier. $O_2(^1\Sigma_g^+)$ is continuously produced in the reactor from $O_2(^1\Delta_g)$, by the well-known energy pooling Reaction 1:

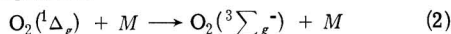


This reaction, as well as others which are second order in $O_2(^1\Delta_g)$, are slow and do not interfere measurably with the first order decay of $O_2(^1\Delta_g)$ under our experimental conditions (2). Removal of $O_2(^1\Sigma_g^+)$ by deactivation at the surface of the reaction chamber, in the gas phase, and by radiation is so fast compared with the decay of its precursor $O_2(^1\Delta_g)$, that steady state kinetics may be applied to calculate the equilibrium concentration of $O_2(^1\Sigma_g^+)$ which is proportional to the square of the $O_2(^1\Delta_g)$ concentration. Thus, the atmospheric band at 7620 Å gives a relative measure of the $O_2(^1\Delta_g)$ concentration. It has been shown that the decay constant $1/\tau_p$, measured at 7620 Å, is related to the $O_2(^1\Delta_g)$ quenching rate constant k_{Mi} of various quenching gases M_i by the relationship

$$1/\tau_p = 2 \left[k_s + k_w + \sum_i k_{Mi} \cdot (M_i) \right]$$

where k_s corresponds to the radiation transition probability of $O_2(^1\Delta_g)$ and k_w is its rate constant of wall deactivation. When all pressures except that of the quencher under consideration, are kept constant, a linear plot between $1/\tau_p$ and M is expected.

Data from a series of experiments with 0.4 torr NO_2 , 7 torr O_2 , and varying pressures of SO_2 , H_2S , CH_3SH , CH_3COCH_3 , CH_2O , ambient air, and synthetic air at room temperature are plotted in Figures 1-3. In each case the expected linear relationship is observed above a certain pressure. The curvature at low pressures of SO_2 , ambient air, and other gases is due to adsorption phenomena which lower k_w . The effect is reversible after prolonged pumping of the reactor. The rate constants calculated from the slopes of the straight lines are summarized in Table I. Some of these may actually represent the sum of two rate constants, k_2 and k_3 , for physical quenching and chemical reaction:



There are some interesting points concerning the quenching efficiencies of these primary and secondary air pollutants. The $O_2(^1\Delta_g)$ has been discussed as a possible

Table I. Rate Constants for Deactivation of $O_2(^1\Delta_g)$ by Some Primary and Secondary Air Pollutants at Room Temperature

Compound	$10^{19} \times k$ (cm^3 molecule $^{-1}$ sec $^{-1}$)		
	This work	Ackerman et al. (9)	Clark and Wayne (13)
SO ₂	0.39 ± 0.09		
H ₂	2.1 ± 0.2		
CH ₃ SH	10 ± 3	38	
CH ₃ COCH ₃	16 ± 4		
CH ₂ O	23 ± 3		
"Ambient air"	3.4 ± 0.4		4.4 ± 1.3
Dry synthetic air	3.0 ± 0.1		

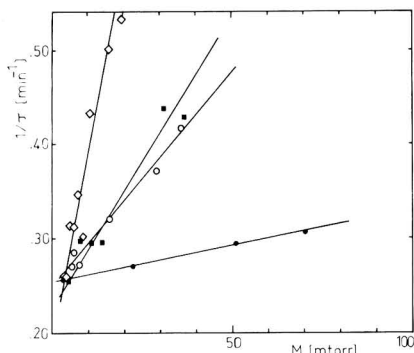


Figure 1. Quenching of $O_2(^1\Delta_g)$ by ● H₂S, ○ CH₃SH, ■ CH₃COCH₃, and ◇ CH₂O; $p(O_2) = 7$ mtorr and $p(NO_2) = 0.4$ mtorr

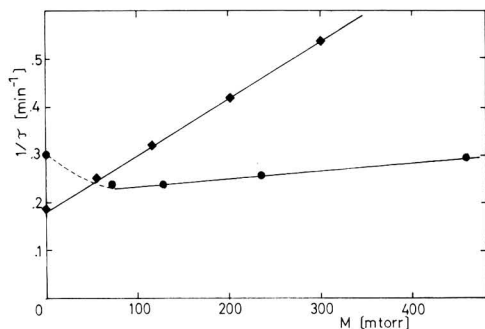


Figure 2. Quenching of $O_2(^1\Delta_g)$ by ● SO₂ and ◆ dry synthetic air; $p(O_2) = 7$ mtorr and 4 mtorr, respectively, and $p(NO_2) = 0.4$ mtorr

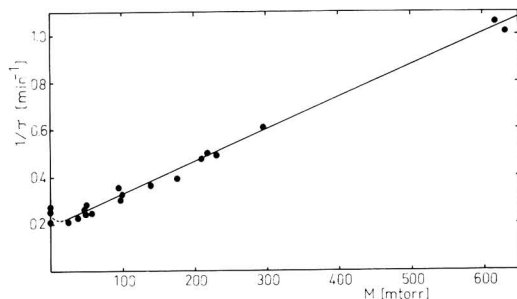


Figure 3. Quenching of $O_2(^1\Delta_g)$ by ambient air; $p(O_2) = 4$ mtorr and $p(NO_2) = 0.3$ mtorr

oxidant of SO₂ in the lower atmosphere (5). Thermodynamically, only Reaction 4 need be considered, since the reaction yielding SO₃ and O(³P) is 13.6 kcal/mol endothermic:



The SO₄ radical has been suggested as an intermediate in the homogeneous atmospheric photooxidation of SO₂ (6). Our data indicate that the quenching of O₂(¹Δ_g) by SO₂ is first order in SO₂ pressure and is extremely slow which excludes the three-body Reaction 4 as an important step of the modification of SO₂ in the atmosphere. It can be shown from our measurements with ambient air and from our previously published rate constants for the quenching of O₂(¹Δ_g) by pure atmospheric gases (2), that in an atmosphere containing 0.1 ppm of SO₂, only one out of 10⁸ singlet oxygen molecules will be quenched by SO₂. A comparison of this figure with the estimated singlet oxygen production rate of 0.5 ppm hr⁻¹ in polluted atmospheres (7, 8) shows clearly that the SO₂ photooxidation must occur via other routes.

Ackerman et al. (9) determined the quenching rate of O₂(¹Δ_g) with various sulfur compounds in a flow system by measuring the intensity of the O₂(¹Δ_g) emission at 1.27 μ along the flow tube. They state that methyl mercaptan is essentially quenched physically. Their rate constant for the quenching of singlet oxygen by CH₃SH, Table I, is higher than our value by nearly a factor of 4. The authors used mercury distillation through the discharge to remove oxygen atoms. We know, however, from previous experiments that HgO alone does not completely remove oxygen atoms from discharged oxygen, since measurable amounts of NO were evolved when oxygen from a Hg/O₂ discharge was introduced into the 220-m³ reactor containing 0.5 mtorr NO₂ as a scavenger.

Furukawa and Ogryzlo (10) observed that traces of oxygen atoms interfere seriously with the determination of rate constants for the quenching of singlet oxygen by organic amines. This interference is due to radicals from reactions of O(³P) atoms with organic compounds, which react with singlet oxygen much more rapidly than stable molecules (Becker et al., to be published). Since no oxygen atoms were present during our decay measurements in a static system, we conclude that our value of the CH₃SH rate constant is correct.

The fact that H₂S is a poorer quencher of O₂(¹Δ_g) than CH₃SH may be attributed to the higher ionization potential of H₂S. A linear correlation between the ionization potentials and the logarithms of the quenching rate constants of amines and sulfur compounds, respectively, has been observed by Ogryzlo and Tang (11) and by Ackerman et al. (9) and was ascribed to charge transfer interaction between quencher and singlet oxygen. Recent work by Furukawa and Ogryzlo (10) indicates that the correlation is more involved than had been previously assumed.

From a number of measurements using "ambient air" from outside the laboratory as a quencher of O₂(¹Δ_g), a rate constant of $(3.4 \pm 0.4) \times 10^{-19}$ cm³ molecule⁻¹ sec⁻¹ was obtained. The partial pressure of water in the atmosphere was calculated from the relative humidity and the temperature to be 18 ± 2 torr at the time of the experiments. To evaluate the influence of humidity on the rate constant, pure dry synthetic air was also used as a quencher, and a rate constant of $(3.0 \pm 0.1) \times 10^{-19}$ cm³ molecule⁻¹ sec⁻¹ was obtained. The difference between the dry and the wet air values is less than would be expected from published data on the quenching of singlet oxygen by water vapor (2, 12). The dry air value is consistent, within the error limits, with a rate constant of (4.4

$\pm 1.3) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ given by Clark and Wayne (13) and with an estimate of $3 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ by Evans et al. (14) to fit measured atmospheric altitude profiles of $\text{O}_2(^1\Delta_g)$. It also agrees fairly well with our published rate constant of $(1.7 \pm 0.1) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for pure oxygen, since nitrogen does not contribute appreciably to the quenching of singlet oxygen in the atmosphere (2). A reinvestigation of the important rate constant $k(\text{O}_2)$, which is not compatible with data of other investigators (12, 13), will be published separately.

The reactivity toward $\text{O}_2(^1\Delta_g)$ of all pollutant molecules listed in Table I is comparable to or lower than that of pure ambient air. Reactions of these contaminant species with atmospheric $\text{O}_2(^1\Delta_g)$ are therefore unimportant. Because these reactions would probably lead to products of a highly oxidizing nature, it is not inconceivable that they may be precursors of or be themselves substances hazardous to health. Up to the present, however, it has not been investigated what products, if any, are produced from the interaction of $\text{O}_2(^1\Delta_g)$ with these molecules and thus no categorical answer as to the toxicological role of $\text{O}_2(^1\Delta_g)$ in air pollution can as yet be given.

Note Added in Proof: A recent publication by Huie and Herron (15) describing results concerning reactions of $\text{O}_2(^1\Delta_g)$ with a wide variety of organic compounds, arrives at essentially the same conclusion concerning the role of excited O_2 in atmospheric processes.

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Received for review November 12, 1973. Accepted May 10, 1974.
Work supported by the Bundesministerium des Innern.

Photochemical Reactivities of Aldehyde-Nitrogen Oxide Systems

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■ The photooxidation of formaldehyde, acetaldehyde, and propionaldehyde in the presence of nitrogen oxides produces the same products and biological effects as do hydrocarbon photooxidations. Despite the greater consumption of formaldehyde, propionaldehyde is generally the most reactive in terms of higher product yields, eye irritation, and plant damage. Product yields from the photooxidation of formaldehyde-nitrogen oxide tends to be the most sensitive to variation in the ratio of reactants. As a result the oxidant yields from the reactions in the formaldehyde-nitrogen oxide system exceed those of the other systems at higher aldehyde-nitrogen oxide ratios. The photochemical reactivities of the three aldehydes in terms of product yields, eye irritation, and plant damage overlap those of the olefinic and aromatic hydrocarbons. The reduction of formaldehyde and higher molecular weight aldehydes should be accomplished along with reduction of hydrocarbons in emission control strategies for photochemically reactive substances.

Aldehydes have been shown to be formed as the result of incomplete combustion in internal combustion engines (1-4), diesel engines (1, 5, 6), and incinerators (3, 7). Aldehydes also are major products of the laboratory photooxidation of olefins and alkylbenzenes in the presence of nitrogen oxides, all in the ppm range in air (8). Atmo-

spheric analyses confirm that aldehydes exist at significant concentrations in the Los Angeles atmosphere as a result of combustion and atmospheric reactions (9-11).

When photooxidized in air with radiation between 2900 and 3500 Å, formaldehyde and other aliphatic aldehydes in the absence of nitrogen oxides react to form products identified as hydrogen peroxide, alkylhydroperoxides, carbon monoxide, and lower-molecular-weight aldehydes, (12, 13), and the intermediates formed can react with olefins and alkylbenzenes (14). When photooxidized in air in the presence of nitrogen oxides, aliphatic aldehydes react rapidly to form oxidants including ozone, hydrogen peroxide, and peroxyacyl nitrates (15-17). These products cause damage to plants (18, 19). Saturated aliphatic aldehydes, when irradiated with nitrogen oxides, also cause eye irritation (15, 18).

The past studies have not involved a systematic investigation of the photooxidation of aldehydes in the presence of nitrogen oxides as a function of aldehyde or nitrogen oxide concentration. In the present work reaction products, eye irritation, and plant damage from the photooxidation of formaldehyde, acetaldehyde, or propionaldehyde with nitrogen oxide have been measured as the concentrations and ratios of reactants are varied. These results are used to achieve three objectives: develop the relationships between aldehyde and nitrogen oxide as reactants with the products or effects measured, compare the photochemical reactivity parameters for the aldehyde systems with each other and with those obtained pre-

viously in the same irradiation chamber for several hydrocarbon-nitrogen oxide systems, consider various mechanistic aspects relevant to aldehyde-nitrogen oxide systems.

Experimental Details

This study was carried out in a 335-ft³ chamber irradiated with a mixture of sunlamps and blue fluorescent and black light fluorescent lamps according to Altshuller et al. (20-22). The radiation distribution and intensity were designed to approximate sunlight. The photodissociation rate of NO₂ in the chamber was 0.4 min.⁻¹. The chamber was operated at a relative humidity of 50% (75°F) and the temperature of the reaction mixture was maintained between 87 and 90°F. The total irradiation period was 5½ hr. The initial charge of nitrogen oxide just before the irradiation started consisted of 90-95% nitric oxide and 5-10% nitrogen dioxide. These experimental conditions also were those used in the previous studies (20-22).

The nitric oxide and the nitrogen dioxide were analyzed by the widely utilized manual colorimetric method for nitrogen dioxide evaluated by Saltzman (23). The nitric oxide was analyzed as nitrogen dioxide after oxidation with Na₂Cr₂O₇-impregnated paper (24).

Formaldehyde was prepared by the thermal dissociation of the β-polymer of formaldehyde. Acetaldehyde and propionaldehyde were redistilled products of K and K Labs and Eastman.

The peroxyacyl nitrates and alkyl nitrates were separated on a 8 ft × ¼ in. (244 × 0.318 cm) borosilicate glass column packed with 10% Carbowax 400 on 60-80 mesh Gas Chrom Z at 25°C, and these products were analyzed by means of an electron capture detector maintained at 80°C.

Formaldehyde was analyzed by the chromotropic acid method after collection in sodium bisulfite solution (25). Acetaldehyde and propionaldehyde were separated by means of a 12 ft × ¼ in. (366 × 0.318 cm) stainless steel column packed with 10% 1,2,3-tris(cyanoethoxy)propane on 60-80 mesh Gas Chrom Z at 70°C and analyzed with a flame ionization detector. "Total" oxidant was measured by the colorimetric neutral KI method and corrected for NO₂ interference.

A number of experiments were conducted with from 5-55 pphm of nitrogen oxide, mostly nitric oxide, added to the chamber and irradiated with no deliberately added aldehyde present in the chamber. With initial nitrogen oxide concentrations of 50-55 pphm, only a few parts per hundred million of oxidant were produced in 6 hr with the corresponding oxidant dosages only 0.02-0.03 ppm/hr. From 30-40% of the half part per million of nitrogen oxide was converted to nitrogen dioxide by the end of the irradiation with the corresponding nitrogen dioxide dosage about 0.6 or 0.7 ppm/hr. With initial nitrogen oxide concentrations of 5-12 pphm, from 8-17 pphm of oxidant was produced with corresponding oxidant dosages of 0.25-0.35 ppm/hr. Irradiations of 8-17 pphm of nitrogen oxide resulted in 50-80% conversions of nitrogen dioxide by the end of the irradiation. No plant damage could be detected from irradiations of nitrogen oxides without deliberately added aldehydes. However, eye irritation panel responses averaged about 0.6 unit to the cleanest irradiated air available.

The oxidants formed at low nitrogen oxide concentrations were sufficient to preclude extrapolation of oxidant concentration or oxidant dosages to zero at zero nitrogen oxide concentration. However, this background contribution does not appear to be significant within the range of nitrogen oxide concentrations used in the aldehyde-nitrogen oxide mixtures. The eye irritation background effect

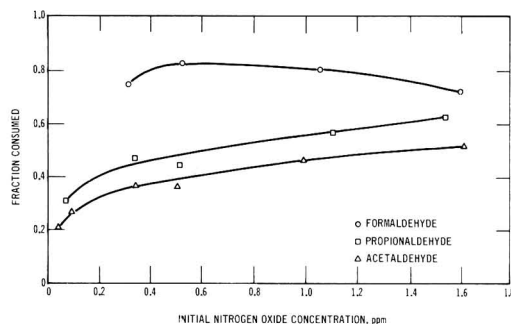


Figure 1. Fractions of aldehyde consumed in a 5½-hr irradiation period as a function of initial nitrogen oxide concentration at initial concentrations of 3 ppm for formaldehyde, acetaldehyde, or propionaldehyde

was significant compared to total eye irritation responses. The averaged background eye irritation response was arbitrarily subtracted from the total responses to obtain the net eye irritation indices reported in this paper.

The reactants in the series of experiments were selected to provide a range of aldehyde concentrations, nitrogen oxide concentrations, and molar ratios of reactants. However, the aldehyde concentrations were adjusted initially as near to 3 ppm as possible for most of the experiments conducted to determine the chemical and biological effects of varying the nitrogen oxide concentration. Correspondingly, the nitrogen oxide concentration was adjusted initially to as near 0.5 ppm as possible for most experiments conducted to determine the chemical and biological effects of varying the aldehyde concentrations. The usual range of molar reactant ratios covered was 2:1 up to 10:1. However, in several experiments at 3 ppm of aldehyde, the nitrogen oxide concentrations were as low as 7 or 8 pphm, corresponding to a molar reactant ratio of 40:1. In a subset of experiments, the effect of a threefold decrease in both reactants on aldehyde consumption and oxidant yield and dosage was measured. Initial concentrations selected were 3 ppm of aldehyde and 1.5 ppm of nitrogen oxide along with 1 ppm of aldehyde and 0.5 ppm of nitrogen oxide.

Chemical Results

Consumption of Aldehydes. The fraction of formaldehyde, acetaldehyde, and propionaldehyde consumed in a 5½-hr irradiation was dependent on the nitrogen oxide concentration at 3 ppm initial concentration of aldehyde—that is, dependent on ratio of reactants—but was almost independent of the absolute concentration of reactants. The reduction of initial nitrogen oxide concentration resulted in a slow but monotonic decrease in consumption of acetaldehyde and propionaldehyde, but the consumption of formaldehyde peaked slightly before beginning to decrease below 0.5 ppm of nitrogen oxide (Figure 1). Although the fraction consumed decreased, a twentyfold decrease in nitrogen oxide from 1.50-0.075 ppm resulted in only a twofold decrease in the amount of acetaldehyde or propionaldehyde consumed (Figure 1). Similar experimental results have been observed for the propylene-nitrogen oxide system (20). At a two-to-one ratio of reactants, a threefold reduction in absolute concentration of reactants resulted in fractional aldehyde consumptions within ±10% for each of the three aldehyde-nitrogen oxide systems. A similar lack of dependence on absolute concentration of reactants at various reactant ratios was reported for the propylene-nitrogen oxide system (20).

Nitrogen Dioxide Formation and Consumption. The time to nitrogen dioxide peak concentration in irradiation of 3 ppm of formaldehyde, acetaldehyde, or propionaldehyde with nitrogen oxide decreased nonlinearly with decreasing initial nitrogen oxide concentration (Figure 2). The order of decreasing time to nitrogen dioxide peak concentration for the three systems over the range of nitrogen oxide concentrations used is as follows: propionaldehyde < formaldehyde < acetaldehyde.

The time to nitrogen dioxide peak concentration in irradiation of 0.5 ppm of nitrogen oxide increases nonlinearly with decreasing concentration of formaldehyde, acetaldehyde, or propionaldehyde (Figure 3). The largest period of time to nitrogen dioxide peak concentration occurs consistently with the acetaldehyde-nitrogen oxide system with a crossover between the formaldehyde-nitrogen oxide and propionaldehyde-nitrogen oxide systems at about 2.2 ppm of aldehyde. The effect of decreasing the initial aldehyde concentration on time to nitrogen dioxide peak concentration varies considerably among the aldehyde-nitrogen oxide systems.

Nitrogen dioxide dosages in ppm \times hr consistently decrease with decreasing nitrogen oxide concentration (Figure 4). The slopes are nearly linear at higher nitrogen oxide concentration levels, but tend to decrease in slope at lower nitrogen oxide concentration levels. The order of increasing nitrogen dioxide dosages for the three systems above 0.5 ppm of initial nitrogen oxide concentration is as follows: acetaldehyde > formaldehyde > propionaldehyde.

Oxidant Yields and Oxidant Dosages. The level of oxidant yields produced from the photooxidation of aldehyde-nitrogen oxide systems is strongly dependent on aldehyde and nitrogen oxide concentration (Figures 5 and 6). At 3 ppm of aldehyde and 1.5 ppm of nitrogen oxides, a 2-to-1 molar ratio of reactants, the order of increasing maximum oxidant yields was as follows: propionaldehyde > acetaldehyde > formaldehyde (Figure 5). For aldehyde concentrations of 3 ppm and at nitrogen oxide concentra-

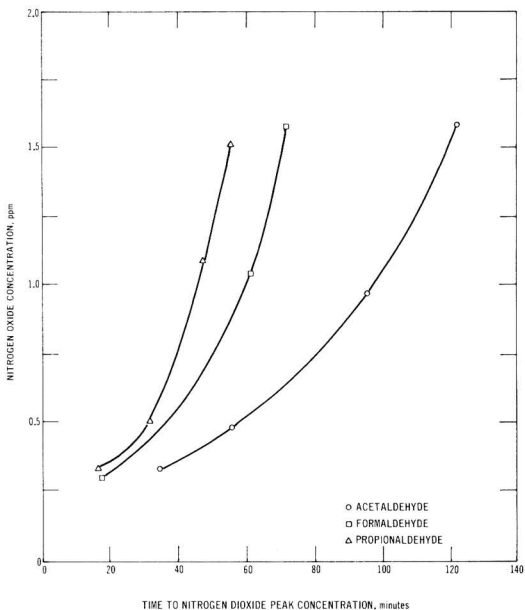


Figure 2. Times of nitrogen dioxide peak concentration as a function of initial nitrogen oxide concentration with initial concentrations of 3 ppm for formaldehyde, acetaldehyde, or propionaldehyde

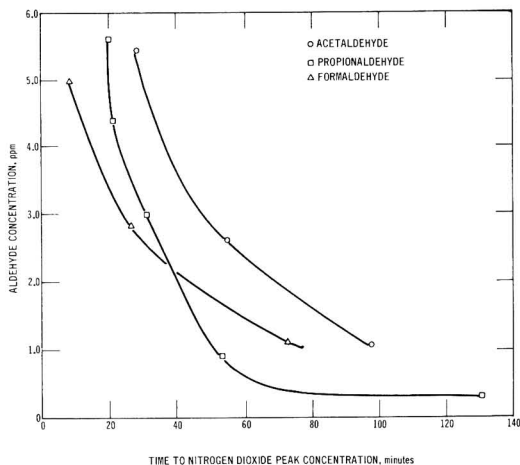


Figure 3. Times of nitrogen dioxide peak concentration as a function of initial formaldehyde, acetaldehyde, or propionaldehyde concentration with initial concentrations of 0.5 ppm for nitrogen oxide

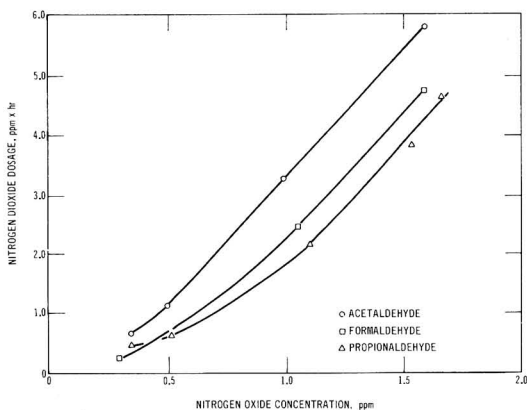


Figure 4. Nitrogen dioxide dosages (ppm/hr) as a function of initial nitrogen oxide concentration with initial concentrations of 3 ppm for formaldehyde, acetaldehyde, or propionaldehyde

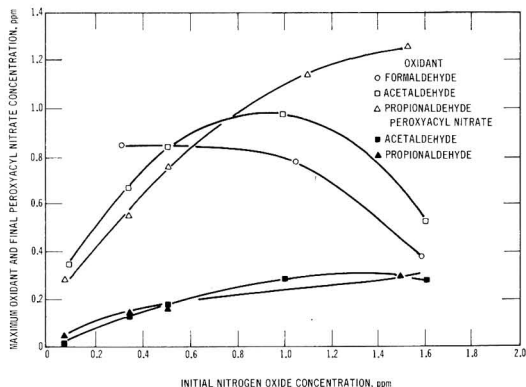


Figure 5. Maximum oxidant concentrations and final peroxyacyl nitrate concentrations as a function of initial nitrogen oxide concentration with initial concentrations of 3 ppm for formaldehyde, acetaldehyde, or propionaldehyde

tions below 0.5 ppm, corresponding to a molar ratio of reactants above 6 to 1, the order of increasing maximum oxidant yields was reversed: formaldehyde > acetaldehyde > propionaldehyde. The oxidant yield from the photooxidation of the formaldehyde–nitrogen oxide system increases with decreasing initial NO_x concentration down to at least 0.3 ppm. Even though the oxidant yields from the acetaldehyde–nitrogen oxide and propionaldehyde–nitrogen oxide photooxidations do decrease below 1 ppm of ni-

trogen oxides with decreasing nitrogen oxide concentration (at constant initial aldehyde concentration), large decreases in nitrogen oxide concentration result in much less than proportional decreases in oxidant yield.

Decreasing aldehyde concentration below 3 ppm results in decreased oxidant yields (Figure 6) for all three aldehydes. However, at acetaldehyde or propionaldehyde concentrations above 3 ppm, the oxidant yields first level off and then decrease somewhat. A similar effect on oxidant yield also was caused by propylene in the study of the propylene–nitrogen oxide system (20).

The oxidant yields were measured at a 2-to-1 molar ratio of reactants at both 3- and 1-ppm concentration levels of each aldehyde. The oxidant yields from photooxidations with the aldehydes at 3 and 1 ppm are as follows: formaldehyde, 45 and 35 pphm; acetaldehyde, 66 and 53 pphm; propionaldehyde, 125 and 71 pphm. Thus, a threefold decrease in concentration of both reactants results in much less than a proportional decrease in oxidant yield.

As for the maximum oxidant concentrations, the oxidant dosages computed are strongly dependent on nitrogen oxide concentration and reactant ratio with an initial aldehyde concentration of 3 ppm (Figures 7 and 8). At a 2-to-1 molar ratio of reactants, the order of increasing oxidant dosages for the three aldehyde–oxide systems was as follows: propionaldehyde > acetaldehyde > formaldehyde. The oxidant dosages computed from photooxidation of the formaldehyde–nitrogen oxide system increased continuously from reactant ratio of 2 to 1 to above 10 to 1 (Figure 7). For the acetaldehyde–nitrogen oxide and the propionaldehyde–nitrogen oxide systems with 3-ppm initial aldehyde concentration, the oxidant dosages increased with increasing reactant ratios, maximized at 6-to-1 molar reactant ratios (nitrogen oxide, 0.5 ppm) and 3-to-1 molar reactant ratios (nitrogen oxide, 1 ppm), respectively, and decreased at higher reactant ratios. Decreasing aldehyde concentration at 0.5-ppm initial nitrogen oxide concentration results in decreasing oxidant dosages (Figure 8). High propionaldehyde concentrations suppress oxidant dosages as well as oxidant yields.

The oxidant dosages at the 2-to-1 molar ratio of reactants with aldehyde and nitrogen oxide concentrations of 3 and 1.5 ppm and 1 and 0.5 ppm, respectively, were as follows: formaldehyde, 1.1, 1.0; acetaldehyde, 1.4, 1.3; propionaldehyde, 3.6, 2.4 ppm \times hr. Thus, a threefold decrease in the concentration of both reactants resulted in much less than a proportional decrease in the corresponding oxidant dosages.

Carbon-Containing Products. The major carbon-containing products identified from the ultraviolet irradiation of the propionaldehyde–nitrogen oxide were acetaldehyde, carbon monoxide, and peroxypropionyl nitrate. The minor carbon-containing products identified included formaldehyde, acetone, methyl ethyl ketone, ethyl nitrate, and peroxyacetyl nitrate. The carbon balances for three typical experiments involving irradiation of propionaldehyde–nitrogen oxide mixtures are given in Table I. The product analyses accounted for from 62–95% of the propionaldehyde consumed with no trend discernible with irradiation time.

From 40–60% of the acetaldehyde consumed in irradiations of acetaldehyde–nitrogen oxide mixtures was converted to peroxyacetyl nitrate and formaldehyde. The minor carbon-containing products identified were acetone and methyl nitrate. Carbon monoxide analyses were not made on this system.

Yields and Dosages of Organic Nitrogen Compounds. The major nitrogen-containing organic compound identified from the ultraviolet irradiation of the propionaldehyde–nitrogen oxide system was peroxypropionyl nitrate

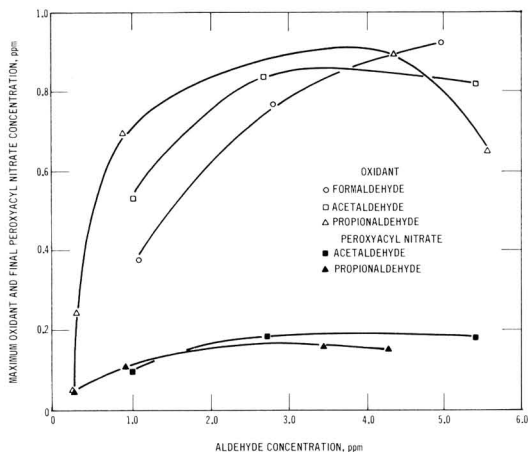


Figure 6. Maximum oxidant concentrations and final peroxyacetyl nitrate concentrations as a function of initial formaldehyde, acetaldehyde, or propionaldehyde concentration with initial concentrations of 0.5 ppm for nitrogen oxide

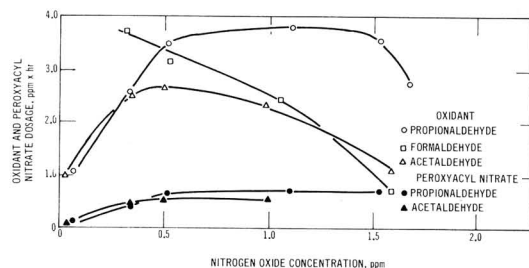


Figure 7. Oxidant and peroxyacetyl nitrate dosages (ppm/hr irradiation) as a function of initial nitrogen oxide concentration with initial concentrations of 3 ppm of formaldehyde, acetaldehyde or propionaldehyde

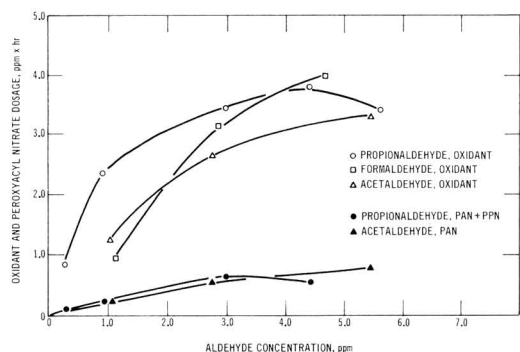


Figure 8. Oxidant and peroxyacetyl nitrate dosages (ppm/hr irradiation) as a function of initial formaldehyde, acetaldehyde, or propionaldehyde concentration with initial concentrations of 0.5 ppm of nitrogen oxide

(Table II). The minor nitrogen-containing organic products identified included peroxyacetyl nitrate and ethyl nitrate. From 22–58% of the nitrogen oxide (nitric oxide and nitrogen dioxide) consumed in the irradiations of the propionaldehyde–nitrogen oxide mixtures was converted to peroxypropionyl nitrate, peroxyacetyl nitrate, and ethyl nitrate. The ratio of peroxypropionyl nitrate to peroxyacetyl nitrate decreased by a factor of two for longer, compared to shorter, irradiation periods. The ratio of peroxypropionyl nitrate to peroxyacetyl nitrate also decreased with increasing initial nitrogen oxide concentration.

The major nitrogen-containing organic compound identified from the ultraviolet irradiation of the acetaldehyde–nitrogen oxide system was peroxyacetyl nitrate with methyl nitrate as a minor product. From 30–46% of the nitrogen oxide (nitric oxide and nitrogen dioxide) consumed in the irradiations of the acetaldehyde–nitrogen oxide mixtures was converted to peroxyacetyl nitrate and methyl nitrate.

The fraction of nitrogen oxide accounted for as nitrogen-containing organic products increased as the initial nitrogen oxide concentration decreased. Similar behavior has been observed previously in studies of the propylene–nitrogen oxide system (20) and of the *m*-xylene–nitrogen oxide system (22).

The peroxyacetyl nitrate and peroxypropionyl nitrate yields tend to decrease either with decreasing nitrogen oxide or aldehyde concentration (Figures 5 and 6). The peroxyacetyl nitrate and peroxypropionyl nitrate dosages, unlike their yields, are almost independent of nitrogen

oxide concentration above 0.5 ppm of nitrogen oxide, but decrease rapidly below 0.5 ppm of nitrogen oxide (Figure 7). These dosages decrease almost linearly with decreasing aldehyde concentration below 3 ppm (Figure 8).

Biological Results

Eye Irritation Index. The eye irritation index used represented the average response for the complete panel for the one or several experiments with a given mixture composition, near the end of the irradiation of the reaction mixture. The index is based on a 0–5 scale. The net eye irritation index is the scale value derived corrected for the panel response to the background air. The indices are given at an initial nitrogen oxide concentration of 0.5 ppm as a function of aldehyde concentration for formaldehyde, acetaldehyde, and propionaldehyde (Figure 9). The eye irritation index increases with molecular weight: propionaldehyde > acetaldehyde > formaldehyde. The index decreases with slightly less than a linear relationship to aldehyde concentration for each of the three aldehydes. The indices also are given at an initial aldehyde concentration of 3 ppm as a function of nitrogen oxide concentration for each of the three aldehydes (Figure 10). Again, the eye irritation index increases with molecular weight of the aldehydes. The index decreases nonlinearly with decreasing nitrogen oxide concentration.

The procedure of measuring eye irritation near the end of the irradiation period tends to underestimate the eye irritation potential of substances such as formaldehyde which are themselves eye irritants. Since 70–80% of the

Table I. Carbon Balance for Atmospheric Photooxidation of Propionaldehyde–Nitrogen Oxide Mixtures

Mixture	Irradiation period, min	Propionaldehyde-consumed carbon atoms, ppm	Ratio of product formed to propionaldehyde consumed, as carbon atoms						
			CO	CH ₂ O	CH ₃ CHO	Ketones	PAN	PPN	Sum ^a
A ^b	120	1.56	0.26	0.00	0.51	ND	0.01	0.16	0.94
	240	2.85	0.22	0.00	0.58	ND	0.01	0.12	0.93
	330	3.81	0.18	0.01	0.53	0.03	0.01	0.09	0.85
B ^c	120	2.40	0.11	0.00	0.41	ND	0.01	0.15	0.68
	240	3.72	0.14	0.00	0.40	ND	0.01	0.11	0.66
	330	4.65	0.16	0.01	0.40	ND	0.01	0.09	0.67
C ^d	120	3.21	0.04	0.03	0.37	0.10	0.01	0.07	0.62
	240	4.86	0.08	0.03	0.44	(0.1)	0.02	0.11	0.78
	330	6.09	0.10	0.03	0.31	0.11	0.02	0.10	0.67

^a Ethyl nitrate yields less than 1% of propionaldehyde consumed. ^b Initial reaction mixture of 2.76 ppm propionaldehyde and 0.30 ppm NO_x. ^c Initial reaction mixture of 3.45 ppm propionaldehyde and 0.47 ppm NO_x. ^d Initial reaction mixture of 3.48 ppm propionaldehyde and 1.47 ppm NO_x.

Table II. Nitrogen Balance for Atmospheric Photooxidation of Propionaldehyde–Nitrogen Oxide and Acetaldehyde–Nitrogen Oxide Mixtures

Mixture	Irradiation period, min	NO + NO ₂ , N atoms, ppm	Ratio of product formed to reactant consumed as nitrogen atoms				
			PAN	PPN	MeONO ₂	EtONO ₂	Sum
A ^a	120	0.19	0.04	0.45	0	0.01	0.50
	240	0.23	0.06	0.47	0	0.01	0.54
	330	0.24	0.09	0.48	0	0.01	0.58
B ^b	120	0.43	0.035	0.27	0	0.005	0.31
	240	0.46	0.05	0.285	0	0.005	0.34
	330	0.47	0.06	0.285	0	0.005	0.35
C ^c	120	0.36	0.04	0.23	0	0.01	0.28
	240	1.04	0.04	0.175	0	0.005	0.22
	330	1.31	0.055	0.16	0	0.005	0.22
D ^d	120	0.22	0.455	0	0.005	0	0.46
	240	0.31	0.425	0	0.005	0	0.43
	330	0.32	0.425	0	0.005	0	0.43
E ^e	120	0.27	0.305	0	0.025	0	0.33
	240	0.69	0.31	0	0.02	0	0.33
	339	1.11	0.29	0	0.01	0	0.30

^a Initial reaction mixture 2.76 ppm propionaldehyde and 0.30 ppm NO_x. ^b Initial reaction mixture 3.45 ppm propionaldehyde and 0.47 ppm NO_x. ^c Initial reaction mixture 3.48 ppm propionaldehyde and 1.47 ppm NO_x. ^d Initial reaction mixture 3.52 ppm acetaldehyde and 0.34 ppm NO_x. ^e Initial reaction mixture 3.21 ppm acetaldehyde and 1.60 ppm NO_x.

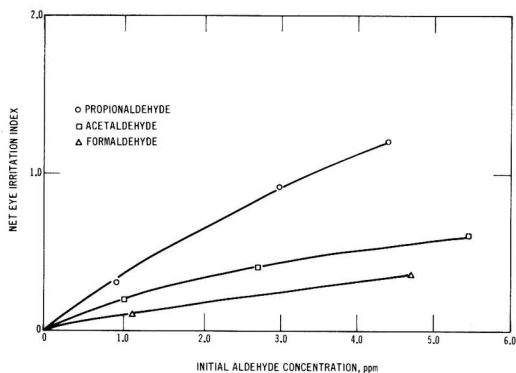


Figure 9. Net eye irritation index as a function of initial formaldehyde, acetaldehyde, or propionaldehyde concentration with initial concentration of 0.5 ppm of nitrogen oxide

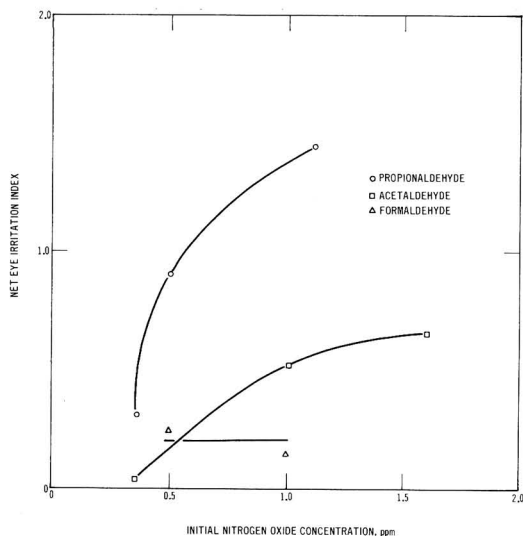


Figure 10. Net eye irritation index as a function of initial nitrogen oxide concentration with initial concentrations of 3 ppm formaldehyde, acetaldehyde, or propionaldehyde

formaldehyde has been converted by the time the eye irritation measurements are made, the average eye irritation over the entire irradiation would be several times greater than near the end of the experiment. Conversely, the eye irritation potential of systems with no initial eye irritation potential is overestimated.

The higher severity of eye irritation response from irradiation of nitrogen oxide with propionaldehyde compared to acetaldehyde or formaldehyde must be caused by a product characteristic of the three-carbon aldehyde. The only product identified that meets this criterion is peroxypropionyl nitrate. The peroxypropionyl nitrate yield from propionaldehyde photooxidation is about equal to the peroxyacetyl nitrate yield from acetaldehyde photooxidation. The formaldehyde and peroxyacetyl nitrate yields are much smaller from propionaldehyde photooxidation than from acetaldehyde photooxidation. If peroxypropionyl nitrate causes the intense eye irritation, it must be much more potent than is peroxyacetyl nitrate or formaldehyde to account for these results.

A quantitative estimate can be obtained if several assumptions are made. It is assumed that the eye irritants

associated with the irradiated formaldehyde-nitrogen oxide, acetaldehyde-nitrogen oxide, and propionaldehyde-nitrogen oxide systems are as follows: formaldehyde; formaldehyde and peroxyacetyl nitrate; formaldehyde, peroxyacetyl nitrate, and peroxypropionyl nitrate. No synergistic effects are assumed to occur among these eye irritants. Solution of simultaneous equations relating the product concentrations of the three eye irritants and the net eye irritation indices for a number of different initial concentrations of reactants resulted in the following eye irritation response factors in terms of index units per ppm of irritant formaldehyde, 0.4; peroxyacetyl nitrate, 1; peroxypropionyl nitrate, 7.

These results are in reasonable agreement with eye irritation measurements on pure components (18). These investigators found acrolein to be two or three times as irritating as formaldehyde; PAN was intermediate between formaldehyde and acrolein. Acetaldehyde itself caused no eye irritation at 5-7 ppm.

Plant Damage. The index used was the average percentage of leaf damage caused to petunia, tobacco wrapper W3, and to old, young, and trifoliate leaves of the pinto bean. Based on this index, the average damage to leaf surfaces from irradiation of 1.0 ppm of propionaldehyde with 0.60 ppm of nitrogen oxides was 75%. In comparison, the average damage to leaf surfaces from irradiation of 1.0 ppm of propylene with 0.60 ppm of nitrogen oxide was 6%. Increasing the concentration levels in the propylene-nitrogen oxide system to 2.0 ppm of propylene and 1.0 ppm of nitrogen oxide and irradiating this mixture caused average damage to leaf surfaces of 24%. Reducing the nitrogen oxide concentration level in the propionaldehyde-nitrogen oxide system to produce a mixture of 1.0 propionaldehyde and 0.05 ppm of nitrogen oxide and irradiating caused average damage to leaf surfaces of 52%. Therefore, the phytotoxicity of the propionaldehyde-nitrogen oxide system is much greater than that attributable to the propylene-nitrogen oxide mixture.

At the 1.0-ppm concentration level of propionaldehyde, varying the initial nitrogen oxide concentration produced a damage to leaf surface curve similar to the oxidant dosage curve. Both curves show a maximum at intermediate nitrogen oxide concentration levels and both oxidant and the damage effects are greatly suppressed at higher nitrogen oxide levels (1.5 ppm). However, at very low nitrogen oxide levels (0.05 ppm), oxidant dosages decrease much more than leaf damage.

Oxidant dosage and peroxyacetyl nitrate dosages for the propylene-nitrogen oxide system are equal to or greater than those for the propionaldehyde-nitrogen oxide system. These plant damage results substantiate the high phytotoxicity of peroxypropionyl nitrate (PPN) compared to ozone or peroxy nitrate (PAN). Taylor (26) concluded that PPN is several times as toxic as PAN. While 0.04 ppm of PAN caused 90% injury in a 4-hr fumigation, 0.01 ppm of PPN caused 100% damage in an 8-hr fumigation to pinto beans.

Photochemical Reactivity Parameters

The experimental results presented in this work are compared in Table III with previous results obtained in the same irradiation chamber for the propylene-nitrogen oxide, *n*-butane-nitrogen oxide, toluene-nitrogen oxide, and *m*-xylene-nitrogen oxide systems (20-22). For each of these five chemical or biological parameters, the yields or effects of the aldehyde-nitrogen oxide systems fall in the range between those previously obtained or exceed those obtained for olefin-nitrogen oxide and alkylbenzene-nitrogen oxide reaction systems.

Of the photochemical reaction parameters considered in the present and past investigations, oxidant dosages (and maximum oxidant concentration) proved to have the most complex relationships to reactant ratios. The oxidant dosages for the three aldehyde-nitrogen oxide systems considered in the present work along with the oxidant dosages from previous investigations for propylene-nitrogen oxide, *n*-butane-nitrogen oxide, toluene-nitrogen oxide, and *m*-xylene-nitrogen oxide (20-22) for reactant ratios between 2 to 1 up to 9 to 1 are tabulated for the seven systems in Table IV.

Three different types of relationships between oxidant dosages and reactant ratios occur for the various organic-nitrogen oxide systems. The oxidant dosage associated with the formaldehyde-nitrogen oxide system is small and for the *n*-butane-nitrogen oxide system is zero at a 2-to-1 reactant ratio, but these dosages increase rapidly to high oxidant dosages at higher reactant ratios. The oxidant dosages associated with the acetaldehyde-nitrogen oxide, propionaldehyde-nitrogen oxide, and the toluene-nitrogen oxide increase more slowly with increasing reactant ratio, reach a maximum at intermediate reactant ratios and decrease again at higher reactant ratios. The oxidant dosages associated with the *m*-xylene-nitrogen oxide and propylene-nitrogen oxide systems decrease continuously with increasing reactant ratio. As a consequence, the oxidant dosages associated with the formaldehyde-nitrogen oxide system equal or exceed those associated with all the other systems at reactant ratios at or above 6 to 1, while this system's oxidant dosage at a reactant ratio of 2 to 1 is much smaller than oxidant dosages associated with the propionaldehyde-*m*-xylene- and propylene-nitrogen oxide systems. The oxidant dosage of the *m*-xylene-nitrogen oxide system exceeds that of the formaldehyde-nitrogen oxide system by over a factor of three at a reactant ratio of 2 to 1, while the oxidant dosage for the *m*-xylene-nitrogen oxide system is less than one half that of the formaldehyde-nitrogen oxide system at a reactant ratio of 9 to 1.

Table V. Percentage of Observed Overall Rate of Reaction Attributable to Aldehyde-Atomic Oxygen Reaction

Aldehyde	Reactant ratio	Stage of reaction, %		
		Early	Intermediate	Late
HCHO	High NO _x concn	0.25	0.6	0.3
	Low NO _x concn	0.5	0.4	≤0.1
CH ₃ CHO	High NO _x concn	1	3	2
	Low NO _x concn	1	1	0.3
CH ₃ CH ₂ CHO	High NO _x concn	0.75	1	0.5
	Low NO _x concn	0.4	0.2	≤0.1

The oxidant dosages tend to differ more at lower than at higher reactant ratios. At the higher reactant ratios, the range of oxidant dosages for the seven systems is less than a factor of three.

The nitrogen dioxide dosages associated with all of the seven systems decrease with increasing reactant ratio, but decrease at different rates. For the formaldehyde-nitrogen oxide system, the nitrogen dioxide dosage decreased by a factor of 17, from 4.4 ppm/hr at a reactant ratio of 2 to 1 to 0.25 ppm × hr at a reactant ratio of 9 to 1 (Figure 4). For the *m*-xylene-nitrogen oxide system, the nitrogen dioxide dosage decreases by a factor of four from 1.2 ppm × hr at a reactant ratio of 2 to 1 to 0.3 ppm × hr at a reactant ratio of 9 to 1 (22). The other five systems exhibit intermediate rates of decrease with increasing reactant ratio.

The variations of peroxyacyl nitrate dosages with increasing reactant ratios are small except for those associated with propylene-nitrogen oxide system. For the propylene-nitrogen oxide system, the peroxyacyl nitrate dosages decrease by a factor of four from 2.0 ppm × hr at a reactant ratio of 2 to 1 to 0.5 ppm × hr at a reactant ratio of 9 to 1 (20), while for the propionaldehyde-nitrogen oxide system the peroxyacyl nitrate dosage was 0.7 ppm × hr at a reactant ratio of 2 to 1 and 0.4 ppm × hr at a reactant ratio of 9 to 1 (Figure 7).

The percentage of organic consumed decreases but slowly, with increasing reactant ratio for all seven systems. Even with very low initial nitrogen oxide concentrations relative to the organic concentration level, substantial percentages of organic are consumed [Figure 1 (20-22)].

Mechanism of Reaction

The reaction of the aldehydes can involve attack by O, O₃, or OH. In addition, the experimental conditions were favorable for photolysis of the aldehydes. Any mechanism of reaction must account for the formation and decay of reactants and products shown in Figures 11 and 12.

The oxygen atom rates of reaction with the aldehydes can be computed. For the oxygen-rich experimental conditions involved, the expression for the atomic oxygen concentration reduces to $[O] = 8 \times 10^{-8} (NO_2)$. The rates $[\Delta RCHO/\Delta t]_0 = K_{RCHO} [O] [RCHO]$ were computed using the following rate constants: HCHO-O, $k = 2.5 \times 10^2 \text{ ppm}^{-1} \text{ min}^{-1}$ (27); CH₃CHO-O, $K = 7.3 \times 10^2 \text{ ppm}^{-1} \text{ min}^{-1}$ (28, 29); and CH₃CH₂CHO-O, $K = 3.4 \times 10^2 \text{ ppm}^{-1} \text{ min}^{-1}$ (30). These rates were calculated at various intervals of time throughout the reactions. The overall observed rates of aldehyde consumption also were computed. The results in terms of percentage of overall rate accounted for as atomic oxygen attack are given in Table V. At no stage in the formaldehyde or propionaldehyde-nitrogen oxide reactions was more than 1% of the overall rate of reaction associated with atomic oxygen reaction in the late stages of reactions involving low initial nitrogen oxide

Table III. Reactivities for Various Photochemical Products and Effects (ppm/hr)

Organic substance	Nitrogen dioxide dosage	Oxidant dosage	PAN dosage	Consumption of organic	Eye irritation index
<i>m</i> -Xylene	0.5	2.4	<0.5	75%	0.5
Toluene	0.65	1.4	0.2	50%	1.4
Formaldehyde	1.4	2.2	0	75%	0.16
Acetaldehyde	1.5	2.15	0.5	42%	0.40
Propionaldehyde	0.9	3.0	0.5	53%	0.65
Propylene	0.7	3.5	1.3	<95%	1.2
<i>n</i> -Butane	1.7	(0.5)	<0.1	18%	0.1

^a For 2 ppm of organic compound and 0.5 ppm of nitrogen oxide.

Table IV. Oxidant Dosages from Photooxidation of Organic Nitrogen Oxide Systems

Organic ^a	Oxidant dosage, ppm/hr, organic to nitrogen oxide molar ratio				
	2 to 1	3 to 1	4 to 1	6 to 1	9 to 1
Formaldehyde ^b	1.1	2.5	2.9	3.3	3.6
Acetaldehyde ^b	1.4	2.3	2.6	2.7	2.4
Propionaldehyde ^b	3.6	3.8	3.7	3.4	2.4
<i>n</i> -Butane ^c	0.0	0.3	0.6	1.3	2.1
Toluene ^d	1.4	1.6	1.6	1.5	1.4
<i>m</i> -Xylene ^d	3.6	2.9	2.6	2.1	1.7
Propylene ^{e, f}	4.0	3.75	3.5	3.0	2.0

^a Initial concentration organic substance, 3 ppm (molar). ^b Present work. ^c Altshuller et al., 1969. ^d Altshuller et al., 1970. ^e Altshuller et al., 1967. ^f Initial concentration, 2 ppm (molar).

concentration levels. Because of the higher acetaldehyde-atomic oxygen rate constant, the maximum contribution of the atomic oxygen reaction was between 2 and 3% of the overall rate for high initial nitrogen oxide in the acetaldehyde-nitrogen oxide irradiations. The results show that the atomic oxygen reactions are not important contributors even at the early stages of reaction. Consequently, very few of the products in any stage of the irradiations for these three systems are formed by atomic oxygen reactions.

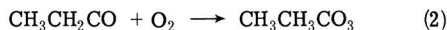
Published rate constants are lacking on the reactions of formaldehyde, acetaldehyde, and propionaldehyde with ozone. Unpublished results on the propionaldehyde-ozone reaction can be used to estimate an upper limit for the rate constant (31). Only an upper limit can be estimated

because the rate of reaction of ozone with propionaldehyde was slower than the rate of surface adsorption by propionaldehyde and of decomposition of ozone. With these limitations, the rate constant is probably equal to or less than 10^{-5} ppm $^{-1}$ min $^{-1}$. Since the propionaldehyde-ozone concentration product does not exceed 1-2 ppm 2 , the rate of reaction cannot exceed $1-2 \times 10^{-5}$ ppm min $^{-1}$. The observed overall rates of reaction for the propionaldehyde-nitrogen oxide irradiations in the stages of reaction where ozone is present at significant levels are $3-5 \times 10^{-3}$ ppm min $^{-1}$. Therefore, the reaction of ozone with propionaldehyde contributes less than 1% to the overall rate of reaction. There is no structural reason why the ozone reactions with formaldehyde or acetaldehyde should be significantly more important.

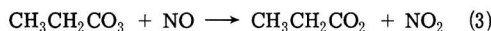
Based on the above discussion, it appears that less than 5% of the overall reactions of these aldehyde systems can be attributed to combined atomic oxygen and ozone reaction. Therefore, the remaining processes involving photolysis and OH reactions must dominate the reactions of aldehydes.

Since the more detailed product distribution results are available for the propionaldehyde-nitrogen oxide irradiation reactions (nitrogen oxide-induced photooxidation), most of the following discussion will concern these results. Most of the products of the propionaldehyde reaction are common to many systems. For example, the propylene-nitrogen oxide irradiations produce most of the same products, including nitrogen dioxide, ozone, carbon monoxide, acetaldehyde, and peroxyacetyl nitrate. Peroxypropionyl nitrate is a somewhat more distinctive product. There is no reason to repeat those reactions usually considered common to a variety of nitrogen oxide-induced photooxidations.

Hydrogen abstraction by OH, or by O, can lead to CH₃CH₂CO. The acyl radical can decompose or add oxygen



The peroxypropionyl radical in the earlier stages of the reaction can oxidize nitric oxide

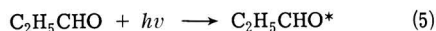


which can be followed by decomposition to the ethyl radical and carbon dioxide:



The photolysis of propionaldehyde favors radical formation rather than stable products (12).

Process I is favored



In the photolysis of propionaldehyde in an oxygen-rich system, the following reaction of the formyl radical appears to be favored (12):



The ethyl radical, a product common to initial reaction by almost all pathways (Reactions 1, 4, and 6), is readily converted to the peroxyethyl radical

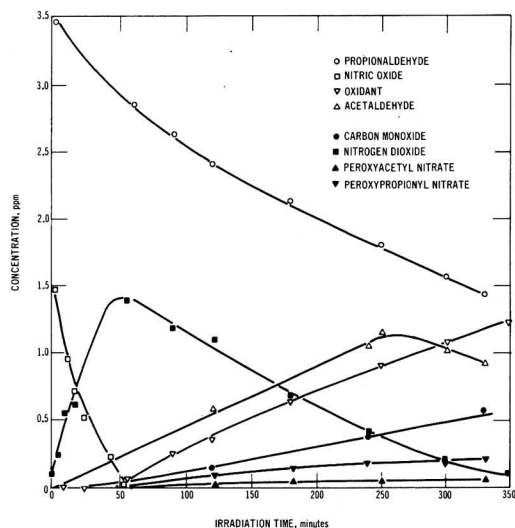
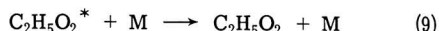


Figure 11. Compositional changes in irradiation of initial mixture of 3.45 ppm of propionaldehyde and 0.47 ppm of nitrogen oxide in air

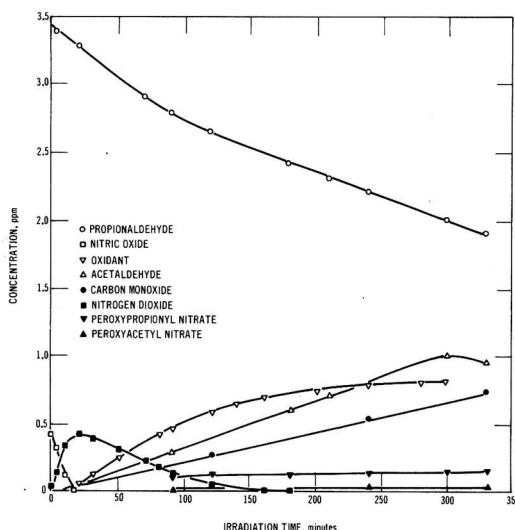
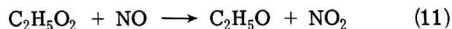


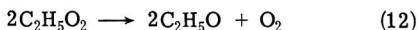
Figure 12. Compositional changes in irradiation of initial mixture of 3.48 ppm propionaldehyde and 1.47 ppm of nitrogen oxide in air

with stabilization by third-body collisions with N_2 and O_2 .

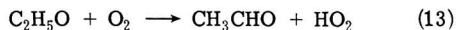
The peroxyethyl radical, as the peroxypropionyl radical, and the HO_2 radical can participate in the oxidation of nitric oxide:



The ethoxy radical also may be formed by the reaction



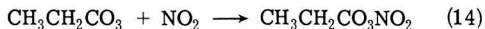
The ethoxy radical can yield acetaldehyde following hydrogen abstraction by oxygen:



Although carbon monoxide is formed as a major product, the yields relative to propionaldehyde consumed still were smaller (0.13–0.79 mol/mol) than the 1.0 and higher yields from propionaldehyde photolysis (12). The acetaldehyde yields relative to propionaldehyde consumed varied from 0.46–0.87 mol/mol, and these yields often exceeded the carbon monoxide yields by factors of 1.5 to 1 up to 2 to 1. The acetaldehyde and especially the carbon monoxide yields increased with decreasing nitrogen oxide concentration (Table I). Despite the higher propionaldehyde consumption at higher nitrogen oxide concentrations, the carbon monoxide yields were lower not only on a mole per mole basis of propionaldehyde consumed, but also on the basis of absolute concentration. These results indicate that the presence of nitrogen oxides suppresses the formation of carbon monoxide. The presence of nitrogen oxide should increase O and OH radical formation and increase rather than decrease carbon monoxide formation by means of Reaction 1. Reactions 5 to 7 produce carbon monoxide, but the presence of nitrogen oxide provides competitive pathways for consumption of propionaldehyde to Reactions 5 and 6.

If Reaction 1 is not significant and if essentially all the carbon monoxide is assumed to arise from Reactions 5 through 7, the carbon monoxide yield can be used to estimate the upper limit for the contribution of the photolysis reactions to the overall reactions. For the various propionaldehyde–nitrogen oxide mixtures with initial reactant ratios of 9.2 to 1, 8.1 to 1, 7.3 to 1, and 2.3 to 1, the fractional contribution of the photolysis reactions to the overall reactions averaged over each of the irradiation periods would be as follows: 0.67, 0.47, 0.41, and 0.22.

The peroxypropionyl radical formed in Reaction 2 can react with nitrogen dioxide to form peroxypropionyl nitrate (PPN):



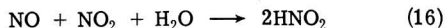
Nitric oxide suppresses PPN formation by reaction with it early in the irradiation period. The peroxypropionyl nitrate yield, relative to propionaldehyde consumed, increases rapidly after the nitric oxide is consumed, but the yield decreases late in the irradiation period. The conversion of the three-carbon acyl radicals to PPN can account for 10–25% of propionaldehyde molecules consumed for various reaction mixtures and irradiation times (Table I, Figures 11 and 12).

Ethyl nitrate always is a minor product with acetaldehyde to ethyl nitrate ratios varying from 100 to 1 up to 500 to 1 for lower initial nitrogen oxide concentrations. Such results indicate that the reaction



is much less important than Reaction 13 or other hydrogen abstraction processes converting ethoxy radical to acetaldehyde.

During the periods of irradiation, before the nitric oxide disappears from the system, satisfactory mass balances are obtained for nitric oxide plus nitrogen dioxide indicating the formation of insignificant concentrations of other nitrogen containing products. The result would not support significant steady state concentration levels of nitrous acid which would require the presence of nitric oxide in its formation by such reactions as

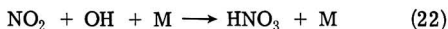
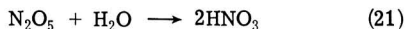
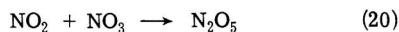


or



The sum of the yields of the organic nitrates never accounts for as much as 60% of the initial nitrogen oxide even when over 90% of the carbon atoms are accounted for as identified products (Tables I and II). Similarly, only 20–30% of the initial nitrogen oxide can be accounted for while 60–70% of the carbon atoms are accounted for as identified products. Such results suggest, as does previous work (32), that much of the nitrogen oxides are converted to nitric acid or inorganic nitrates rather than organic nitrates.

If nitric acid is formed, the following reactions should be significant steps in its formation



Aldehydes are major photooxidation products of the hydrocarbon–nitrogen oxide systems, particularly of olefin–nitrogen oxide systems. Formaldehyde is almost always observed as a product while the presence of other aldehydes depends on the specific hydrocarbon structures. The aldehydes usually begin to be produced at the beginning of the irradiation periods, and they are formed in increasing amounts as the hydrocarbon is depleted. Photooxidation of such aldehyde products also can form lower-molecular-weight aldehydes later in the reaction. For example, photooxidation of propionaldehyde will form acetaldehyde as a product which, in turn, will produce formaldehyde as a product. Aldehydes can be the predominant organic species in the later stages of some hydrocarbon–nitrogen oxide reactions. These aldehydes will participate in formation of ozone, peroxyacyl nitrates, as well as other aldehydes. Photolysis of the aldehydes is a source of radical intermediates influencing the course of reaction. Therefore, the present results should have direct application to the development of adequate mechanisms for hydrocarbon–nitrogen oxide photooxidation reactions.

Conclusions

Measurements of the photooxidations of the three aliphatic aldehydes, formaldehyde, acetaldehyde, propionaldehyde, with nitrogen oxides show that these systems produce similar product yields and biological effects to hydrocarbon–nitrogen oxide systems. At high ratios of reactants, these aldehydes participate in forming yields of ox-

dants exceeding those produced by hydrocarbons such as propylene, toluene, or *m*-xylene. Propionaldehyde-nitrogen oxide mixtures photooxidize to produce substantial levels of eye irritants and phytotoxicants. Thus, aldehydes are as important as hydrocarbons on a molar basis in contributing to the manifestations of photochemical air pollution.

Aldehydes are important products in the nitrogen oxide-induced photooxidation of many hydrocarbons. Both the direct photolysis and the nitrogen oxide-induced photooxidation of aldehydes contribute to the later stages of reaction.

Since aldehydes are both primary (directly emitted) and secondary (photochemical formed) products, their substantial reactivities are of especial importance. Aldehydes will be present early in the day as directly emitted products and later in the day as products of hydrocarbons that will be depleted. Therefore, aldehydes may be expected to contribute to photochemical air pollution problems, not only in the central city, but in the urban, suburban, and rural areas downwind. It seems reasonable to conclude that aldehydes will have the potential for contributing markedly to area-wide exposures of man, animals, and vegetation.

The results of this study suggest several considerations relevant to air pollution control strategies. Since formaldehyde and higher aldehydes are in the same range of photochemical reactivities as olefins and alkylbenzenes, aldehydes demand as much control in source emissions as do hydrocarbons. As combustion processes are modified or add-on combustion control devices are utilized, it is just as important to follow the changes in aldehyde concentrations as the changes in hydrocarbon concentrations. The flame ionization analyzers utilized as monitoring instruments do not normally respond to formaldehyde, and these analyzers respond to higher aldehydes to a lesser extent than the corresponding hydrocarbons. In addition, unless heated lines are used, the higher aldehydes can easily be lost on the surfaces of inlet systems. Therefore, the monitoring techniques for hydrocarbons do not respond proportionately to aldehydes. Consequently, adequate monitoring instruments are needed for aldehyde measurements in source emissions and in the ambient air.

Substantial efforts are being made to develop and improve photochemical models to serve as predictive tools in evaluating air pollution strategies for implementation planning. In view of the importance of aldehydes both as reactants and products, such models should be able adequately to predict the concentration variations of aldehydes as well as products such as ozone and nitrogen dioxide.

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Received for review April 19, 1973. Accepted May 17, 1974.

Biodegradability of Photodegraded Polymers

I. Development of Experimental Procedures

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■ Methods have been developed to study the biological oxidation of plastic fragments in natural soils and sewage sludge using a modification of the conventional Warburg apparatus. Rates of biodegradation are estimated from the consumption of oxygen under carefully controlled conditions. Whereas high-molecular-weight plastic particles are shown to be resistant to biodegradation, degraded branched polyethylene and polypropylene show significant rates of oxidation in both environments. Degraded polystyrene appears to be more resistant to microbial attack.

Recently a method has been developed for making many types of plastics photodegradable [Guillet (1)]. Several of these are being commercialized under the trade name Ecolyte to provide a solution to the serious problem of littering in a throwaway society. These plastics disintegrate (lose their structural strength and thus are subject to mechanical breakdown) under the influence of ultraviolet irradiation. It is clear, however, that a breakdown which is purely physical is not sufficient to return the synthetic materials to the natural carbon cycle.

It is known, however, that when a substance is broken down to a fine powder (by photodegradation or mechanical grinding), it will normally be more readily available for biological recycling to carbon dioxide and water by microbial cells under aerobic conditions. Furthermore, the photodegradation results in a substantial reduction in the molecular weight of the plastic which should improve the possibility of microbial attack. This study was undertaken to determine generally if photodegraded plastic fragments are subsequently available for further biological breakdown through the action of the natural microbial flora of soil and activated sludge from a municipal sewage treatment plant. This paper describes methods suitable for the evaluation of the biodegradability of such materials.

Experimental Methods

Respiration of the microbial flora in soil was taken as the most satisfactory and readily measurable parameter to determine the activity of the organisms capable of metabolizing the breakdown of fragments of the plastic. Two methods were used for these studies: The first was designed to test biodegradability in natural soil; the second was designed to determine the biodegradability of the plastic residues under conditions similar to those occurring in a sewage treatment plant.

Procedure for Soil Tests. The first tests were conducted in "Hach" respirometers where the bottles were charged with different soils and quantities of various plas-

tics residues, sealed, and the oxygen consumption was measured by the change in pressure in the bottles, the evolved CO₂ being absorbed by a KOH solution. A control sample was run to determine the "natural" oxygen uptake of the soil with no added carbon source. By difference it was possible to determine (a) if the plastic increased the oxygen uptake rate, indicating biodegradation of the plastic; or (b) if no change in oxygen uptake rate occurred, then the plastic was not being degraded microbiologically; or finally (c) if a reduction in oxygen uptake rate was observed, it might be deduced that the plastic was having an inhibiting effect of some kind. Under the conditions of the tests, the plastic will show virtually no oxygen uptake due to autooxidation.

Garden soil was collected in April 1972, and forest and land-fill soils were collected in June 1972. The soils were air-dried in the laboratory, screened to less than 2-mm diameter, and were then stored in glass bottles at 5°C.

At the beginning of the experiments, the substrates (plastic powders) were added directly to the soil which was then wetted to 60% of its maximum water-holding capacity. In a later experiment the moisture loss was determined every two weeks and was compensated for by adding sterile distilled water. In this experiment, the KOH solution was also replaced each week.

The pH was determined on suspensions with soil-water ratio of 1:2.5 and water-holding capacity was determined by the method of Coutts (2). Total nitrogen was determined on 2.0 grams of garden soil and forest soil, and on 5.0 grams of land-fill soil, using semimicro Kjeldahl method with CuSO₄·H₂O as catalyst and modified with salicylic acid to include nitrate as described by Cole and Parks (3). Organic matter and organic carbon were determined by the wet combustion method. The characteristics of the different soils used in these experiments are shown in Table I.

Activated Sludge Procedure. This series of experiments was conducted to determine the rate of biodegradability of the plastics in an aqueous environment such as a sewage treatment plant or a natural water body.

Mixed liquor was collected from the Humber Sewage Treatment Plant, Toronto. A Warburg Respirometer was used to measure O₂ uptake. A 2.0-ml sample of mixed li-

Table I. Properties of Soils Used

	Organic matter, %	Total nitrogen, %	pH	Water-holding capacity	C:N ratio
Garden soil	3.47	0.1036	7.8	35.71	20
Forest soil	11.04	0.1365	6.5	56.53	47
Land-fill soil	2.16	0.0658	8.2	30.0	19

quor was placed in the main chamber of a conventional Warburg flask. Accordion pleated pieces of filter paper were inserted in the central well and 2.0 ml of 20% potassium hydroxide was added. The flasks were then attached to their respective manometers and were placed in a water bath at 20°C. Plastic powders (1% w/v) were added directly to the mixed liquor. Manometric determinations of O₂ uptake were carried out by the "direct method" [Umbreit et al. (4)].

Materials

Four materials were used in these experiments.

Polypropylene. A sample of Ecolyte PP polypropylene film (1 mil) was allowed to photodegrade under artificial ultraviolet radiation until it became extremely fragile and could be broken up under finger pressure into small fragments. This was then ground to a fine powder for soil tests. The number average molecular weight of the photodegraded plastic was 2200 (by ebulliometry). The infrared spectrum (Figure 1a) shows evidence of substantial photo-oxidation as indicated by carbonyl bands at 5.83 μ .

Polyethylene. To obtain a large sample of material suitable for testing, the polymer used was a polyethylene resin prepared by thermal degradation of low-density polyethylene, followed by air oxidation to introduce carbonyl groups. The number average molecular weight of this polymer was 2300 by ebulliometry. The infrared spectrum is shown in Figure 1b. This sample is expected to be similar in structure and molecular weight to fragments produced in the photodegradation of plastics such as Ecolyte PE. The sample was ground to a fine powder for soil tests (<200 mesh).

Polystyrene. 1. Polystyrene was prepared from styrene monomer using a peroxide catalyst in an emulsion bead polymerization procedure. The polymer was ground to 200 mesh for soil tests. 2. A sample of Ecolyte PS polystyrene was molded into thin films and exposed for 72 hr in an American Ultraviolet Co. uv accelerometer. It was then ground to a fine powder, <200 mesh, for soil tests. The number average molecular weight of this sample was 15,000.

Elemental analyses of the three degraded polymers used are summarized in Table II.

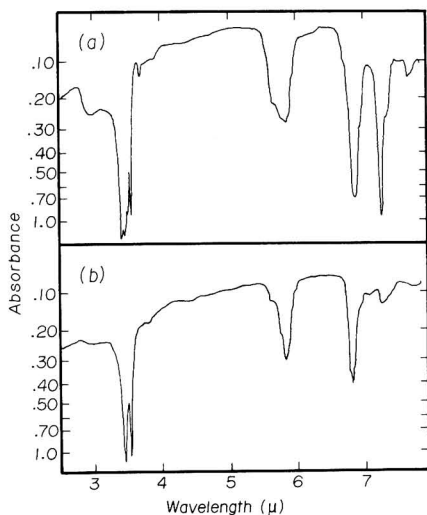


Figure 1. Infrared absorption spectrum of (a) photodegraded polypropylene (sample EP), and (b) degraded, oxidized polyethylene (sample EE)

Table II. Analytical Data of Degraded Polymer Samples

Sample	C, %	H, %	O, %
Polypropylene	79.22	13.45	7.52
Polyethylene	82.14	13.45	4.47
Polystyrene	91.76	7.79	0.54

Results and Discussion

Soil Control Experiments. Figure 2 shows the rate of oxygen uptake of the garden soil control, measured sequentially over approximately a six-month period. In each case the sample shows an accelerated absorption of oxygen over the first three to four days, and then a nearly linear absorption over periods of up to two months. In the first two series of trials, a break in the linear part of the curve took place at the end of about one month, indicating some change in the experimental conditions. In the third series the KOH solution was replaced every week, and the moisture content of the soil maintained constant; in this case the linear portion of the curve was extended to 70 days. For this reason the results of the first two series are considered to be reliable only for the first 28 days of the tests.

The slope of the linear portion of the curves in Figure 2 decreases as the series progresses (series 1 = 1.5 ml/day, series 2 = 1.35 ml/day and series 3 = 1.2 ml/day). This is attributed to the loss of microbial activity of the soil with storage at 5°C. Since the experiments were run consecutively, series 3 had the longest storage time. The relative activity of the three soil samples used, as measured by oxygen uptake, is shown in Figure 3. The forest soil is by far the most active whereas land-fill soil is the least active. The activities seem to correlate with the carbon content of the soil, although the acidity as measured by pH is also different.

Polypropylene. Oxygen uptake data on photodegraded polypropylene (EP) in garden soil are shown in Figure 4 along with data on degraded polyethylene (EE). Although the rate of oxygen uptake is considerably less for the polypropylene than for polyethylene, both plastic samples are clearly contributing to the biochemical oxygen demand of the soil. Similar results are obtained for forest soil and for land-fill soil. The increase in oxygen utilization over that of the soil control is shown for the three different soil samples in Figure 5. There is an initial rapid oxygen uptake during a period of about 20 days after which the rate decreases. However, it is interesting to note that the rate continues at a much greater value in land-fill soil, which had the lowest natural carbon content, than in forest soil which already contained a relatively high content of organic carbon. Over the 70-day period of the test, the net oxygen uptake due to the presence of the plastic residues in the soil was 3.7, 4.2, and 5% of theory for the forest, garden, and land-fill soils, respectively.

These results are also in apparent contradiction to those of Potts et al. (5) who reported that branched hydrocarbons were not biodegradable. However, Potts et al. (5) used only a small selection of fungi (not bacteria) in their tests, and furthermore most of their polymers were not oxidized to introduce carbonyl groups.

Our results clearly show that the photodegraded polypropylene is being biologically oxidized in natural soil conditions. If the rate of oxidation were to continue at approximately the same value, one could expect nearly complete biodegradation of the sample in about four years.

Polyethylene. Oxygen uptake data on degraded polyethylene (EE) in garden soil are shown in Figures 4 and 7. It is clear that the polyethylene fragments are oxidized more rapidly than those from polypropylene, and over the

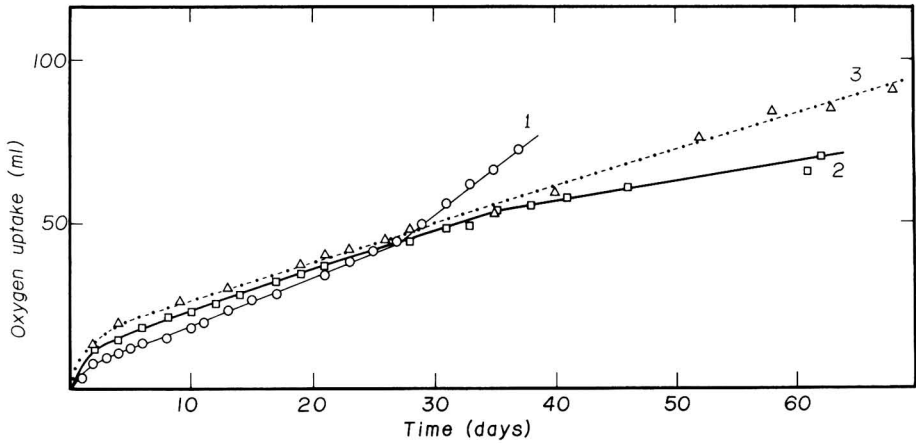


Figure 2. Oxygen uptake for garden soil controls

70-day period of the test, about 9% of the theoretical amount of oxygen has been absorbed. This effect is the opposite to that expected from the normal susceptibility of these polymers to chemical oxidation, since it is known that polyethylene, being a more linear hydrocarbon, is less readily oxidized than polypropylene. However the results are consistent with what is known about the biological oxidation of such materials, since it is well established that linear hydrocarbon chains are more readily metabolized by microorganisms.

From our tests it seems incontrovertible that natural soils contain a variety of organisms capable of carrying out the biooxidation of fragments of photodegraded polyethylene and polypropylene.

Polystyrene. Oxygen uptake data from similar experiments using polystyrene powder and photodegraded Ecolyte PS have been made. Over the 30-day period of the test there appeared to be no difference from the control within experimental error, indicating that the biodegradation of the plastic samples, if it occurs, is too slow to measure by this test. The photodegraded sample showed a slight re-

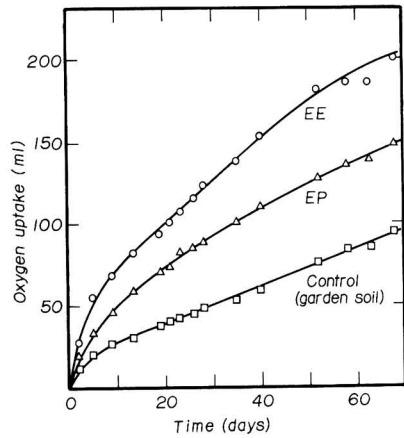


Figure 4. Oxygen uptake of plastic residues in garden soil

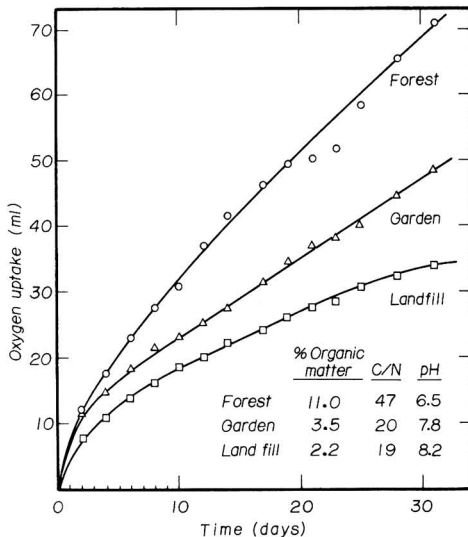


Figure 3. Oxygen uptake for control samples of various soils

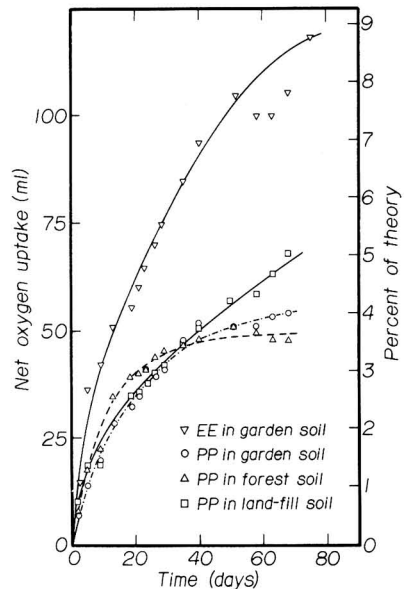


Figure 5. Net oxygen uptake of plastic residues in various soils

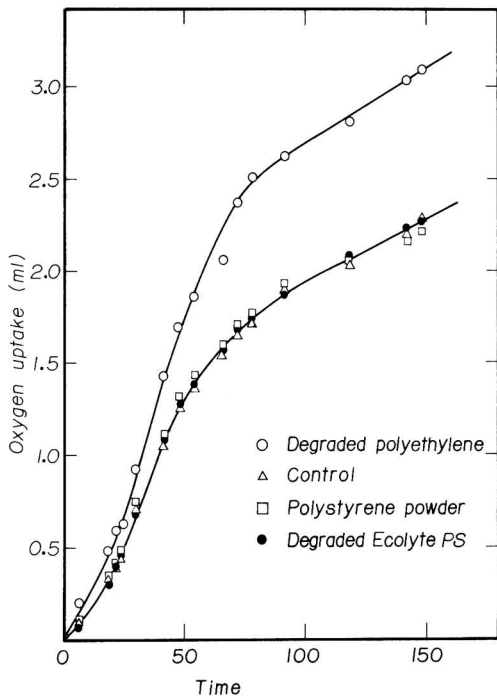


Figure 6. Oxygen uptake of polymers in sewage sludge

tardation of oxygen uptake toward the end of the period, but it is not clear from these tests whether this effect is outside the usual experimental error for this procedure. In any case, no similar retardation was observed in the sewage sludge method. The molecular structure of polystyrene consists of a long hydrocarbon chain containing phenyl groups every second carbon atom. Similar structures occur naturally, for example in lignins in wood, and are known to biodegrade much more slowly than cellulose for example. It is therefore not surprising that the rapid biodegradation observed with polyethylene and polypropylene residues does not occur with polystyrene. However, it seems likely that a slow rate of biodegradation should occur even with polystyrene fragments, but more sensitive procedures will be required to observe this process.

Sewage Sludge Tests. Results of oxygen uptake using sewage sludge in a Warburg apparatus are shown in Figure 6. Degradation of organic carbon already in the sludge gives rise to oxygen consumption as shown in the control sample. Both polystyrene powder and photodegraded Ecolyte PS showed identical values to the control sample, but polyethylene residues showed a marked increase in oxygen uptake. The difference from the control for polyethylene and polypropylene is shown graphically in Figure 7. Oxygen uptake for the polyethylene sample is initiated immediately and increases rapidly for about 70 hr, after which the oxygen utilized indicates that 2% of the theoretical value for complete oxidation of the polyethylene. On the other hand, for polypropylene there is an induction period of about 20 hr followed by a period of rapid acceleration up to about 80 hr. The rate slows down thereafter and about 1% of the theoretical amount of oxygen is consumed in the 150-hr period of the test. The slowing down at the end of the period appears to be a characteristic of the test, since the addition of fresh sludge to the sample will initiate further rapid oxidation.

The sewage sludge tests therefore confirm the results of

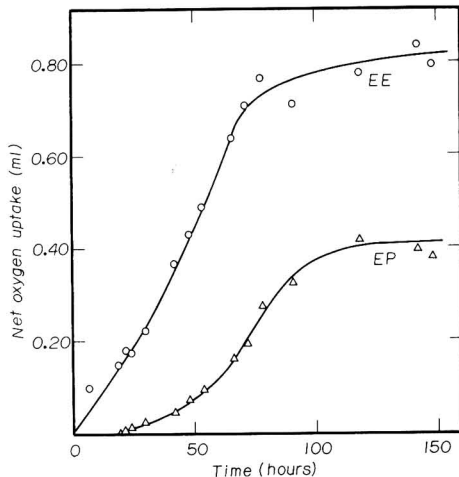


Figure 7. Net oxygen uptake of polyethylene (EE) and polypropylene (EP) residues in sewage sludge

the soil tests, but it is evident that the rate of biodegradation in this concentrated culture of microorganisms is about ten times as fast as observed in natural soil. Both polyethylene and polypropylene residues are biologically oxidized in these tests but no measurable biodegradation is observed for the polystyrene samples.

Another interesting feature is the rapid initial rate for polyethylene as compared with the lag period for polypropylene. This suggests that the microorganisms required for the biodegradation of linear hydrocarbons such as polyethylene are already present in substantial quantities in sewage sludge. However, it seems likely that microorganisms capable of metabolizing the branched chain hydrocarbons from polypropylene required time to develop the necessary enzymes in order to metabolize branched chains. Additional information on the isolation and identification of these microorganisms will appear later in this series of papers.

An interesting point brought out by this series of experiments is that these plastic materials are degraded faster in sewage sludge than in various types of soils. The removal of the compounds in soil from solution is affected by soil texture, particularly by the clay in the sample. The slow degradation in soil may result from adsorption of the substrates, but possibly of greater importance is the partial inactivation of enzymes by certain clays, an effect which has greater significance because the enzyme or enzyme system is extracellular and, therefore, it can have its activity altered by clays [Alexander (6)]. Enzyme inactivation and substrate adsorption phenomena may account, at least in part, for the slower microbial degradation of plastics in soils. However, in sewage sludge other factors such as the high concentration of nutrients, enough dissolved O_2 , pH, and so forth, may be operative and therefore the high decay rate might be expected.

The lower degradation rate of plastics in soils could also be due to the limiting of certain nutrients such as nitrogen and phosphorus. The statement that a soil has 3.1% organic matter or 0.14% nitrogen does not mean that these quantities are readily available to microorganisms. Only a small portion of the total organic carbon or nitrogen is utilized by the microflora each year, the rest remains as a slowly available reservoir. Therefore, the level of organic matter or nitrogen reflects more a potential than an actual supply. It is only the available nutrient which is of im-

mediate significance to microorganisms [Alexander (6)]. Since the addition of the plastic materials in the soils might have increased the nitrogen demand, the slow degradation is to be expected. Probably, the degradation may be stimulated by supplemental nitrogen. This aspect will form a further area of study.

Conclusions

From the results of these tests it is concluded that fragments produced by the degradation of polyethylene and polypropylene in the presence of oxygen are biologically oxidized both in natural soil and in an aqueous sewage sludge environment. The rate of degradation is much more rapid in sewage sludge than in soil, but these results indicate that if the degradation fragments are in the form of a fine powder, biodegradation should occur in approximately one year in natural soils. Fragments from degraded polystyrene appear to be more resistant to biodegradation.

Determination of the rates of such biodegradation will probably require the use of trace methods.

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Received for review December 10, 1973. Accepted May 24, 1974. This research was supported by EcoPlastics Limited, Thornhill, Ont., Canada, and the National Research Council of Canada.

Biodegradability of Photodegraded Polymers

II. Tracer Studies of Biooxidation of Ecolyte PS Polystyrene

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■ The biological oxidation of a photodegraded polystyrene-vinyl ketone copolymer has been examined using a radioactive tracer technique. The evolution of radioactive carbon dioxide from the copolymer in both soil and an activated sewage sludge environment has been monitored. The results show that the photodegraded copolymer is considerably more biodegradable than the undegraded polymer. The rate of biodegradation observed is slow, but this is not unexpected in view of the known slow rates of biological degradation of lignin and other natural products containing aromatic residues. The tests show that the degraded polymers are attacked by soil microorganisms at measurable rates but the technique is not suitable for longer term tests due to a natural leveling off of bacterial activity in the closed systems used.

In Part I (page 919), it was demonstrated that degraded fragments of polyethylene and polypropylene were oxidized biologically by microorganisms in natural soil and sewage sludge to give carbon dioxide and water. However, using photodegraded polystyrene (Ecolyte PS) resulted in no significant difference between the rate of CO₂ production in the presence and absence of the plastic. It was concluded that in the case of polystyrene, the rate of oxidation was too slow to detect by this method. The present studies were carried out to employ tracer methods to see if any biodegradation was occurring at all under these conditions.

Experimental

Soil and Activated Sludge Samples. The samples used were the sample of garden soil and activated sludge described in Part I.

Polymers. Styrene α -¹⁴C and styrene β -¹⁴C were obtained from Mallinckrodt and diluted with purified styrene monomer. Copolymers were made using this diluted monomer with approximately 5% vinyl ketone by a bulk polymerization for 72 hr at 75°C using benzoyl peroxide as catalyst. The polymers were purified by dissolving in toluene and precipitation in methanol. This procedure was repeated three times and the polymer was then air dried for 24 hr at room temperature. The residual monomer was assayed by gas chromatography and found to be less than 0.01% in both cases. Polymer properties are summarized in Table I.

Photodegradation. The polymers were pressed into thin films approximately 0.20 mm thick and irradiated in a uv accelerator. After irradiation the samples were slightly yellow and very brittle. The viscosity molecular weight was between 10,000 and 32,000 in each case. The polymers were then ground in a micromill to a particle size less than 200 mesh and stored in brown glass bottles before testing. The sample used in the sewage sludge

Table I. Analytical Data on Polymers Used

	Sample A, polystyrene- α - ¹⁴ C- 5% vinyl ketone	Sample B, polystyrene- β - ¹⁴ C- 5% vinyl ketone
Yield	40 g (40%)	86 g (86%)
Initial molecular weight, M_n	795,300	450,000
Irradiation time	188 hr (method 1) 158.9 hr (method 2)	137 hr (method 2)
Molecular weight after irradiation, M_n	32,200 (method 1) 15,000 (method 2)	31,250 (method 2)
Radioactivity	2.165×10^6 dis/min	1.752×10^6 dis/min
% residual monomer	<0.01%	<0.01%

studies was exposed outdoors in Toronto for three months. Its viscosity average molecular weight was 14,000.

Counting Procedure. Scintillation counting of the radioactive ^{14}C was done in a Nuclear-Chicago Mark III liquid scintillation counter apparatus in a toluene-fluor scintillator solution containing 4 g/l. of 2,5-diphenyloxazole (Ppo) (Amersham/Searle) and 50 mg/l. of 1,4-bis[2,5-phenyloxazolyl]benzene (Popop) (Amersham/Searle).

Determination of Biodegradation of Garden Soil. Two methods of monitoring the $^{14}\text{CO}_2$ output were used. In the first method, 50 grams of garden soil, 1 gram of labeled copolymer, and enough water to bring up the moisture level to 60% of the water-holding capacity of the soil was placed in a 250-ml flask. A test tube filled with 2 ml of NCS solution (a mixture of a quaternary ammonium base in toluene developed as a CO_2 absorbent by Amersham/Searle) was also placed in the flask. The flask was sealed from the outside environment and allowed to stand at room temperature for one week. At the end of the seven days, the NCS solution was replaced with a fresh solution and the flask resealed. The used NCS solution was prepared for scintillation counting by diluting with 10 ml of the toluene-fluor mixture (described above) and placing in a scintillation vial. This was done for irradiated and nonirradiated samples of the α - ^{14}C polymer over a period of eight weeks. The total amount of $^{14}\text{CO}_2$ absorbed over this period was equivalent to 0.238% of the total radioactivity of the polystyrene in the soil. For the nonirradiated sample, less than 0.01% was absorbed as $^{14}\text{CO}_2$ over the same period. The greatest period of activity was over the first 14 days after which a considerable decrease in the amount of $^{14}\text{CO}_2$ given off was observed. This decrease is probably due to three factors: the volatile toluene in the NCS acting as a biostat, the anaerobic conditions developing over the period, and the oxidation of the remainder of the available carbon. Thus a second method was developed in which the radioactive CO_2 was flushed from the flask with air.

The procedure was similar to the previous experiment except that the NCS solution was placed in a gas absorption tube outside the flask. At the end of each week a slow stream of air was flushed through the system and bubbled through the NCS solution, thus absorbing all the $^{14}\text{CO}_2$.

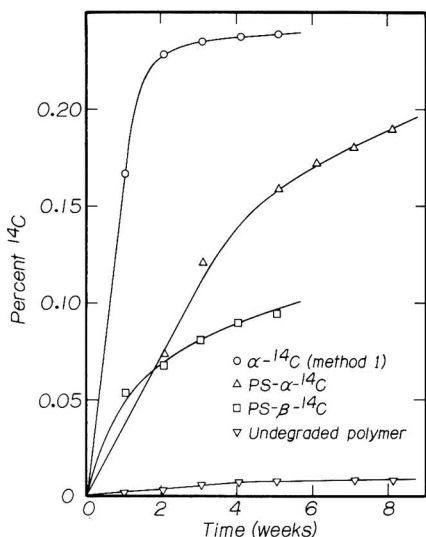


Figure 1. Formation of $^{14}\text{CO}_2$ from biochemical oxidation of labeled Ecolyte PS samples in garden soil

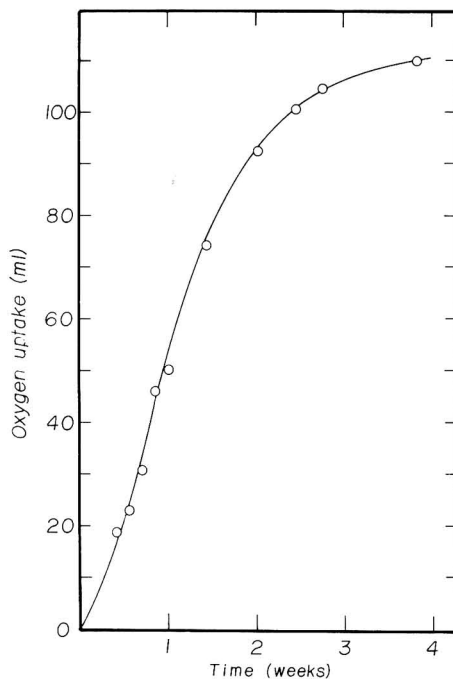


Figure 2. Oxygen uptake for garden soil control

This experiment was carried out for both α - and β - ^{14}C polymers over a period of 70 and 42 days, respectively.

Determination of the Biodegradation of Activated Sludge. A weighed amount of α - ^{14}C polymer and 15 ml of activated sludge were placed in a 50-ml flask equipped with a magnetic stirring bar. The flask was sealed and stirred continuously at room temperature (21–23°C). After each 24-hr period the flask was flushed with air, and the CO_2 was trapped in a NCS solution contained in a gas absorption tube. The NCS solution was removed daily and replaced with a fresh solution. The solution was prepared for scintillation counting as described in the previous section.

Results and Discussion

The results obtained on the two series of trials for the garden soil samples are shown in Figure 1. In the first method the activity of the soil had been reduced so that the biological oxidation terminated after about two weeks. Probably this was due to the toluene vapor present in the flask. The second method appears to give more reliable results. However, the rate of oxidation as represented by the slope of the curve in Figure 2 is slower than in the previous tests. All of the tests show a decrease in the rate of oxidation after about two weeks. This appears to be a characteristic of the experimental techniques since the O_2 uptake of the soil itself (from existing organic carbon) also shows a retardation after two weeks (Figure 2). The trends observed with garden soil appear also for the biooxidation of polymers in activated sludge. The reduction in rate appears to be due to a natural retardation of bacterial activity since, upon addition of fresh sludge to the system, the formation of $^{14}\text{CO}_2$ begins again. This is shown in Figure 3; the addition of fresh sludge was repeated several times. Eventually the rate slows down, possibly due to a buildup in waste products of the bacterial colonies, or to a depletion of the most readily accessible polymer fragments. It

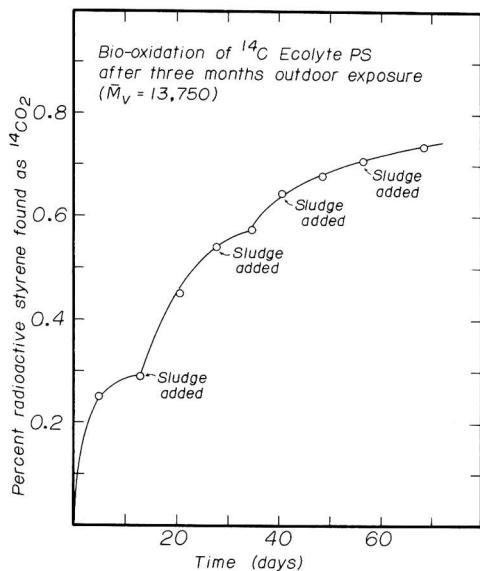


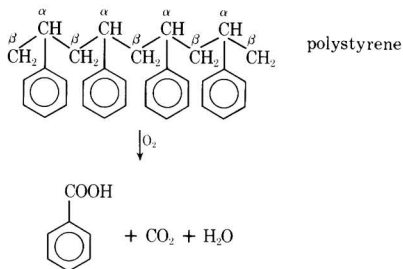
Figure 3. Formation of $^{14}\text{CO}_2$ from biochemical oxidation of photo-degraded ^{14}C -labeled Ecolyte PS in sewage sludge

is probably that in a self-sustaining environment the polymer would continue to degrade biologically until completion of the process. Tests such as these, however, are not suitable for longer term trials because of the natural retardation of bacterial growth in static systems of this kind.

The amount of radioactive $^{14}\text{CO}_2$ formed is clearly much greater for the photo-degraded polymer than for the undegraded polymer in all cases. In the undegraded control, the slow formation of radioactivity appears to level off at about the level of residual monomer, suggesting that it is the monomer being oxidized rather than the polymer. From this we can conclude that the fragments of polystyrene produced in the photooxidation of Ecolyte PS are more biodegradable than the undegraded plastic. Estimates of the time required for complete biodegradation obviously cannot be made from such limited data in the

early stages of the degradation. However, if the rates observed here are approximately representative of the process for the entire period of biodegradation, complete oxidation by microorganisms would require periods of from 20 to 80 years in garden soil and from 11 to 24 years in activated sludge. This is similar to the rates observed for certain natural products, such as the lignins in tropical wood.

The rates of oxidation observed here can be considered only a minimum estimate of the process. The biooxidation of polystyrene is expected to yield fragments such as benzoic acid which may be used directly by microorganisms and not converted to CO_2 :



Normally oxidation is expected at the α -carbon to give benzoic acid, while oxidation of the β -carbon might give CO_2 and water. For this reason it is surprising that the yield of $^{14}\text{CO}_2$ was lower for the β -labeled polymer than for the α -labeled material. Although benzoic acid can be considered a biocide under some conditions, it is commonly implicated as an intermediate in the biooxidation of lignin and other aromatic natural products. It is obvious that further research is necessary before these and other questions regarding the biodegradation of polystyrene can be elucidated.

Acknowledgment

The assistance of M. A. Packham for the scintillation counting is gratefully acknowledged.

Received for review December 10, 1973. Accepted May 24, 1974. Work supported by the National Research Council of Canada under a PRAI grant.

Pressure Drop and Corrosion in Zinc Filters for Mercury Removal from Waste Streams

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The electrochemical displacement reactor is a classical tool of analytical chemistry and it is used to reduce chemical species with oxidation potentials below that of zinc (1). The conventional form of the reactor is a packed column filled with zinc powder, and the solution to be treated is passed through the column by gravity flow. Zinc is a strong reducing agent with a normal half-cell potential of -0.76 V vs. NHE (2), and it is potentially capable of reducing a variety of metal ions present in industrial waste streams.

The most important use of the electrochemical displacement reactor is in the metal industry where it is used to recover copper from solution in a packed scrap iron fil-

ter (cementation technique). The technique has been described (3) as a means to remove mercuric ions from chlor-alkali plant waste brines, but no systematic description is available in the literature of the operational characteristics of such units. The purpose of this report is to provide some information on the possible use of a zinc displacement reactor to remove mercuric ions from industrial waste streams.

Experimental Techniques

The characteristics were studied of an electrochemical displacement reactor packed with zinc for the removal of dissolved mercuric ions from a dilute salt solution. The

pilot reactor was assembled according to the schematic diagram of Figure 1. The processing unit was constructed from polyethylene tanks, PVC piping and pump, and polymethylmethacrylate column materials to eliminate corrosion couples. Flow rates were measured with a calibrated Fischer and Porter rotameter, and the pressure drop across the packed bed was measured with a mercury manometer and with calibrated Bourdon gauges.

Various grades of zinc powder were used, including the New Jersey Zinc Co. grade no. 1206 from which the 30/40 mesh fraction was collected and used for the experiments reported in this paper. The zinc particles were irregular in shape, Figure 2, and microscopic analyses gave an average particle diameter of 0.05 μm . To study the effect of partial mercury saturation on the behavior of the packed bed, experiments were performed with a 10% amalgamated zinc powder. The amalgamation was carried out by immersing the zinc powder in a pH 4 solution of mercuric acetate containing sufficient mercuric salt to give a 10 wt % mercury content in the final dry powder. The coarsest zinc packing used consisted of zinc shot obtained from Fisher Scientific (no. Z-12). The particles were dis-shaped and had an average diameter of 0.5 cm.

The active packing material was supported by a polypropylene screen above an inert packing made from 0.3-cm spherical glass beads. The powders were packed into the column by means of a standard shaking regime using an electric motor with an eccentric load on the shaft to shake a frame to which the column was clamped during the filling operation. The packed height and diameter were 3.2 and 1.7 cm, respectively.

The solutions were prepared with deionized water from a Barnstead deionizer and technical grade sodium chloride (Fisher Scientific No. S-270). The pH of the solutions was adjusted with AR grade hydrochloric acid and sodium hydroxide, and the pH was measured with a Beckman pH meter that was calibrated routinely with solutions prepared from Coleman certified buffer tablets. The viscosities and densities of the solutions were determined by means of a Cannon-Fenske viscosimeter and a Westphal balance, respectively, at ambient temperatures.

The amount of zinc consumed in a particular run was determined by weighing the zinc before and after the run. To remove the zinc oxide and/or hydroxide attached to the zinc powder, all the samples were washed in a 1M NH_4Cl , 1M NH_4OH solution, rinsed in distilled water, and dried with acetone both before and after a run. All the runs were performed at room temperatures between 70 and 82°F.

Experimental Results

The experimental conditions were chosen to reflect an industrial situation of current interest. The solutions contained 5% NaCl, the acidity ranged between pH 5 and pH 8, the mercuric ion concentrations were less than 1 ppm, and the stream temperatures were close to ambient temperatures.

The experimental plan comprised the determination of the hydraulic characteristics of the packed column, the determination of the rate of reaction of the packing material, and studies of the kinetics of the mercuric ion reduction under various conditions. This paper is concerned with the first two aspects of the investigations.

Since the electrochemical displacement reaction is a heterogeneous reaction, and since the mercuric ions were present in a low concentration, it was desirable to use a zinc powder fine enough to provide a large surface area per unit volume to enhance the reaction, yet coarse enough to prevent carryover of fines. The effect of the par-

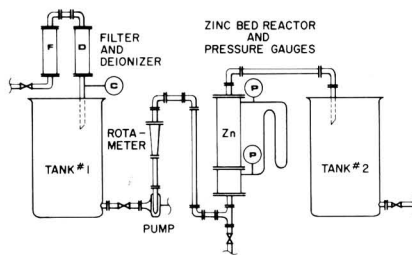


Figure 1. Schematic diagram of waste treatment pilot reactor

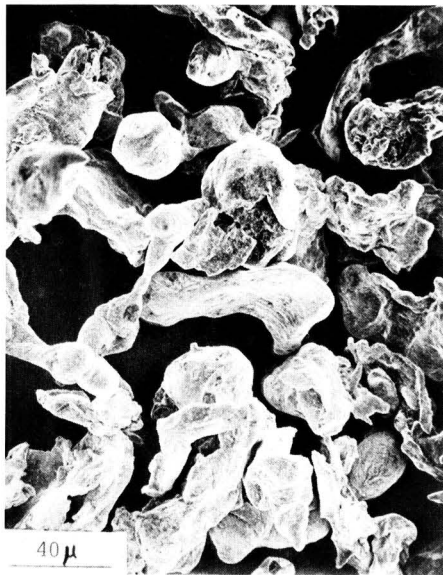


Figure 2. Scanning electron micrograph of zinc powder

ticule size on the adsorption efficiency was demonstrated during preliminary studies with various grades of zinc powder and an illustrative set of data is given in Figure 3. The coarse zinc packing removed less than 20% of the dissolved mercuric ions at all reasonable flow rates, and the 30/40 mesh zinc packing removed more than 95% of the dissolved mercuric salt for residence times of 2 sec or more. Since finer zinc powders gave noticeable carryover, the 30/40 mesh powder was selected as the most suitable packing material.

The experimental results for the first set of pressure drop measurements are shown in Figure 4A for a flow rate of 2500 gal/ft² hr for solutions with a pH of pH5, pH7, and pH8. It may be seen that the pressure drops increased markedly during the runs, and more so at pH5 than in the neutral and the alkaline solutions. The initial pressure drops were the same for all the solutions, 6.6 psi/ft. During the first 5 hr of operation it increased to 23 psi/ft for the pH 5 solution and to about 16 psi/ft for the pH 7 and pH 8 solutions. The effect of a 10% mercury loading is indicated in Figure 4B for the same solutions and the same flow rate. The initial pressure drops were approximately 7.2 psi/ft, the same for all the solutions and slightly greater than in the absence of mercury. The rate of increase of the pressure drops was greater than formerly; it rose to 37 psi/ft after 3 hr for the pH 5 solution and to about 22 psi/ft after 5 hr for the pH 7 and pH 8 solutions.

The amount of mercury deposited on the zinc during

■ Mercuric ions were removed from a simulated waste stream by spontaneous electrochemical deposition on zinc in a flow system. The pressure drop across the zinc filter agreed with Ergun's correlation, and it increased with time due to the accumulation of an insoluble zinc corrosion product in the filter. The increase in the pressure drop was practically eliminated by the use of a zinc ion complexing agent. The rate of corrosion of the zinc was

increased by the complexing agent, and it appeared to be controlled by the rate of mass transfer of a dissolved zinc species in solution. Although the mercuric ion concentrations can be reduced to the low ppb range by the use of zinc filters, the concentration of soluble zinc corrosion products needs to be controlled in applications of the process.

the runs was negligible and could not account for the observed pressure increase with time. The spontaneous reactivity of zinc, on the other hand, was expected to lead to the formation of zinc hydroxide that might obstruct the flow in the packed bed. Observations indicated that the zinc did acquire a white coating during the runs, and subsequent analyses showed that the zinc did react to a significant extent due to the corrosive nature of the solutions.

The excessive pressure buildup was an obstacle to the use of the zinc as an exchange medium, and attempts were made to find an additive that would complex with the zinc ions to maintain a clean zinc surface during the runs. Imidazole proved to be a satisfactory complexing agent (4), and several runs were made to determine its effectiveness in reducing the pressure drop. The results for the pure zinc powder are shown in Figure 4C. In the presence of imidazole the pressure drops decreased at first from their initial values and became practically constant

at values that depended principally on the flow rates. The initial values agreed reasonably well with those observed in the absence of imidazole, 5.0 psi/ft compared with 6.6 psi/ft for the latter, and were essentially independent of the pH. The initial decreases of the pressure drops occurred during the first hour of operation of the beds and amounted to less than 25%. At a flow rate of 2500 gal/hr ft² the pressure drops leveled at about 5.0 psi/ft, independent of the pH between pH 5 and pH 8 and remained at this value during the 5-hr runs. At the lower flow rate of 1250 gal/hr ft², the pressure drops amounted to about 2.0 psi/ft and remained practically constant during the runs. At the higher flow rate of 4470 gal/hr. ft², the pressure drop increased gradually from 13 psi/ft after the initial decrease at a rate of about 1.1 psi/ft, hr.

The effect of a partial bed saturation was explored by using the 30/40 mesh zinc as a packing after it had been amalgamated to contain 10 wt % mercury. The results are shown in Figure 4D and it may be seen that the same patterns prevailed as with pure zinc, except for the pH 7 results that displayed an accentuated time effect. At the lowest flow rate, 1250 gal/hr ft², the pressure drop remained practically constant at 1.8 psi/ft during the runs, as for the pure zinc, and at 2500 gal/hr ft², a pressure drop of 4.0 psi/ft was obtained at pH 5 and pH 8. The pH 7 pressure drop increased gradually during the run at an average rate of about 0.9 psi/ft hr. At the highest flow rate, 4470 gal/hr ft², and at pH 7, the pressure drop increased more markedly with time than it did with pure zinc, rising at an average rate of 2.2 psi/ft hr.

The efficacy of the imidazole in decreasing the pressure buildup in the zinc reactor was attributed to the complexation-dissolution of the zinc species formed when the zinc corroded. Data were obtained on the rate of zinc corrosion by operating the column for various periods of time at a constant flow rate and determining the amount of residual zinc in the column after each run.

The zinc consumption data are given in Figure 5 for conditions corresponding to those used for the pressure drop measurements. The straight lines in the figures are the least square representations of the points shown. If the reaction is assumed to be of zeroth order, the slopes of the least square straight lines give the zeroth order rate constants shown in Figure 6. The rate of the reaction of pure zinc decreased noticeably with an increase in pH, changing from $1.5 \times 10^{-4} \text{ min}^{-1}$ at pH 5 to $0.6 \times 10^{-4} \text{ min}^{-1}$ at pH 8 for a flow rate of 2500 gal/hr ft² in a 1/4-in. thick bed packed to a porosity of 66% with the 30/40 mesh zinc powder. The corrosion rate was slightly lower in the amalgamated bed, being $1.3 \times 10^{-4} \text{ min}^{-1}$ at pH 5 and $0.43 \times 10^{-4} \text{ min}^{-1}$ at pH 8.

The addition of the complexing agent increased the corrosion rates at pH 5 and pH 7, but not noticeably at pH 8. The rates were $2.2 \times 10^{-4} \text{ min}^{-1}$ at the lower pH value and $0.7 \times 10^{-4} \text{ min}^{-1}$ at pH 8. The flow rate exerted a strong influence on the rate of the corrosion reaction. Figure 7. At pH 7 the rate increased linearly from $1.9 \times 10^{-4} \text{ min}^{-1}$ at 1250 gal/hr ft² to $3.4 \times 10^{-4} \text{ min}^{-1}$ at 4470 gal/

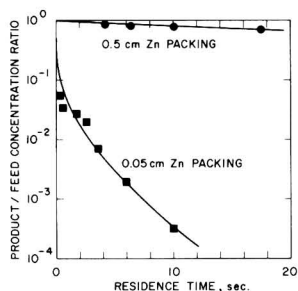


Figure 3. Effect of zinc particle size on adsorption efficiency
Feed: 0.20 ppm Hg²⁺, 5% NaCl, pH 7.0

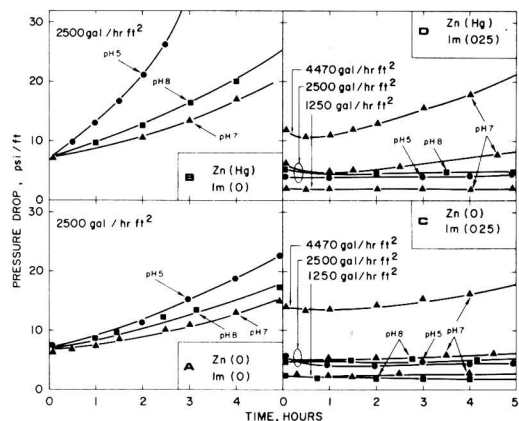


Figure 4. Development of pressure drop in adsorber
Zn(O), pure zinc packing. Zn(Hg), 10 wt % amalgamated zinc packing.
Im(O), imidazole free solution. Im(O25), 0.025 wt % imidazole in solution

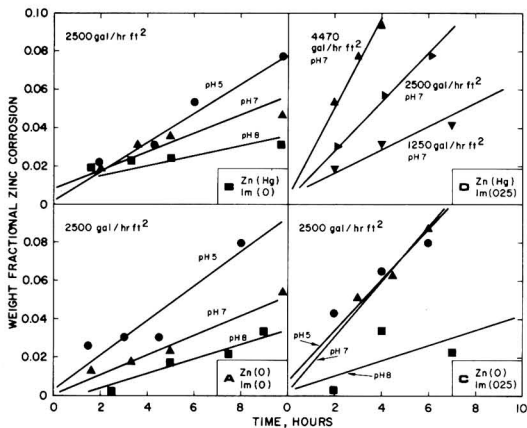


Figure 5. Corrosion of zinc packing

Zn(O), pure zinc packing. Zn(Hg), 10 wt % amalgamated zinc packing. Im(O), imidazole free solution. Im(O25), 0.025 wt % imidazole in solution

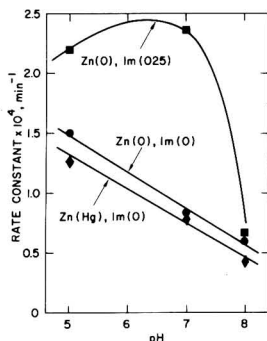


Figure 6. Effect of pH on corrosion rate

Flow rate, 2500 gal/hr ft². Zn(O), pure zinc packing. Zn(Hg), 10 wt % amalgamated zinc packing. Im(O), imidazole free solution. Im(O25), 0.025 wt % imidazole in solution

hr ft² for the pure zinc. Amalgamation appeared to enhance the effect of the flow rate on the corrosion reaction. At 1250 gal/hr ft² the rate was $1.0 \times 10^{-4} \text{ min}^{-1}$ and at 4470 gal/hr ft² it was $3.9 \times 10^{-4} \text{ min}^{-1}$, both at pH 7.

Discussion

The experimental results show that a zinc filter can scavenge mercuric ions from solution efficiently under suitable operating conditions. However, two problems are associated with the use of a zinc filter. The corrosion of the zinc leads to the accumulation of an insoluble corrosion product in the filter that causes a pressure buildup and the power required to operate the filter may become excessive. If the pressure buildup is eliminated by the use of a complexing agent to dissolve the corrosion product, the problem is introduced of an excessive corrosion and discharge of zinc in the effluent, zinc itself being a pollutant. The latter problem may be solved, at least partially, by reconditioning the filter periodically via a separate processing loop. This would generate a concentrated zinc ion solution or a slurry that would need a separate treatment to collect the zinc waste. The recovery of mercury from a zinc filter can be accomplished in a straightforward manner by retorting, this being a process practised on an industrial scale at the present time to recover mercury from a zinc amalgam.

The main concern of this report is the pressure drop in the zinc filter and the corrosion of the zinc. These topics will be discussed below.

The Pressure Drop. The pressure drop in the filter may be discussed with reference to Ergun's correlation for packed beds (5):

$$\frac{\Delta P}{L} = \left[\frac{150(1-E)\mu}{D} + 1.75 G \right] \frac{1-E}{E^3} \frac{G}{\rho g D}$$

where

- ΔP = pressure drop
- L = thickness of filter
- E = filter porosity
- μ = solution viscosity
- D = zinc particle diameter
- G = mass flow rate
- ρ = solution density
- g = gravitational acceleration

The porosity of the filter at the start of the runs prior to the formation of the corrosion product, 66%, was calculated from the volume and weight of the zinc filter and the density of zinc. The viscosity and density of the solutions were 1.15 cP and 1.03 g/cm³, respectively, with small deviations, $\pm 5\%$, from these values as the composition of the solutions changed. The density of the amalgam was within 5% of that of the zinc metal. The calculated and observed pressure drops are shown in Table I. Since the initial pressure drops were practically independent of the pH, the average observed values of the pressure drops over the pH range are shown. The experimental values exceeded the calculated values by a factor of 12.1. This corresponds to a Carman-type shape factor (6) of 0.28 which is close to the value for Berl saddles (0.3). An examination of Figure 2 shows that the zinc particles do bear a resemblance to Berl saddles, and it may be concluded that the zinc filter displays a normal hydraulic behavior.

The essential elimination of the pressure buildup by the use of the zinc ion complexing agent indicated that the pressure buildup was caused by the accumulation of a zinc salt in the filter. The composition of the precipitated salt was not determined, but it is plausible to assume it to be zinc hydroxide. The hydroxide is thought to be the stable species in neutral and near-neutral solutions (7) although the presence of an oxychloride cannot be excluded in chloride solutions (8). Ergun's correlation may be used to estimate the effects of the accumulating precipitate on the pressure drop in terms of the decreasing porosity of the zinc filter. It was observed that the zinc hydroxide settled very slowly when suspended in the test solutions. This indicated that the specific gravity of the hydroxide particles was closer to unity than to the crystallographic value of 3.05, and the former value should be used in calculating the porosity of the partially corroded filter. When we use the maximum observed zinc reaction rate for the pH 5 runs at 2500 gal/hr ft² and a zinc hydroxide effective density of 1.06 g/cm³, a fractional void volume of 52% is obtained after 5 hr of filtration, and this decreased porosity gives an increase in the pressure drop corresponding to the observed value for the pure zinc filter, an increase of 270%. This estimate indicates that the pressure drop of the zinc filter and its change with time are essentially predictable for the imidazole-free solutions.

The principal effect of the imidazole on the pressure buildup was to keep the pressure almost constant during the runs. The slight decrease in pressure at the start of the runs may be attributed to the removal of small amounts of zinc hydroxide from the surface of the zinc at the start of each run. The moderate increase in pressure

Table I. Comparison of Observed and Calculated Initial Pressure Drops

Packing, % Hg	Solution, % imid.	Flow rate, gal/hr ft ²	Pressure drop		
			Observed, psi/ft	Ergun eq. no shape factor, psi/ft	Ergun eq. with shape factor, psi/ft
0	0	2500	6.6	0.50	6.0
10	0	2500	7.2	0.50	6.0
0	0.025	1250	3.0	0.21	2.5
0	0.025	2500	5.0	0.50	6.0
0	0.025	4470	13.4	1.10	13.0
10	0.025	1250	2.0	0.21	2.5
10	0.025	2500	5.0	0.50	6.0
10	0.025	4470	12.0	1.10	13.0

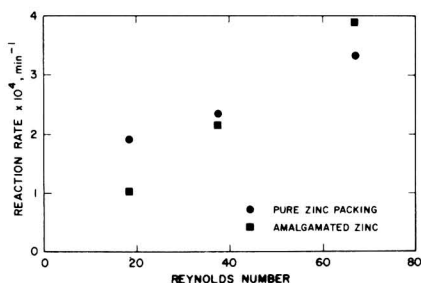


Figure 7. Effect of flow rate on corrosion rate
0.025 wt % imidazole, 5% NaCl, pH 7.0

drop with time was greater for the amalgamated zinc than for the pure zinc, and it was more pronounced at pH 7 than at pH 5 and pH 8. The corrosion rate was greater in the presence of imidazole than in its absence, and it appeared to reach a maximum value near pH 7. The higher corrosion rate at pH 7 may be expected to lead to a more rapid development of the surface roughness and to the observed more rapid pressure buildup.

Zinc Corrosion Reaction. The observed rate of corrosion exceeded that attributable to the mercuric ion/zinc exchange reaction by a factor of 40 or more, assuming 100% exchange of a 0.2 ppm Hg²⁺ solution, and the corrosion reaction may be discussed, therefore, without reference to the exchange process.

Data published by Chatalov and presented by Pourbaix (7) show that the zinc corrosion rate has a minimum near pH 10 in chloride-free solutions, increasing at both higher and lower pH values. This coincides with the Zn(OH)₂ solubility minimum near pH 9 (7) and suggests that the rate-limiting step is diffusion of a species through the hydroxide film on the zinc surface. The enhanced corrosion rate in the presence of imidazole agrees with this interpretation. The thin passivating oxide film known to be present on zinc in alkaline solutions (9) is a possible cause of the failure of imidazole to increase the corrosion rate at pH 8. No attempt will be made to discuss the rate of the corrosion reaction in a quantitative manner for the case of the hydroxide or oxide coated zinc filter. The rate of the reaction in the absence of such a film may be discussed, however, in some detail. The rate of the reaction increased markedly at pH 7 as the flow rate increased, Figure 7, indicating that the diffusion of a dissolved species was the rate-controlling step in the corrosion process in the presence of imidazole.

The liquid phase mass transfer in a packed bed may be described by Richter's equation (10):

$$\frac{Sh}{Re Sc^{1/3}} \cdot \frac{s}{0.12 + E} = \frac{3.72}{Re^{2/3}} + \frac{1.06}{30 + Re^{1/3}}$$

where Sh = Sherwood number
Re = Reynolds number
Sc = Schmidt number
s = shape factor
E = porosity

which in conjunction with:

$\dot{m} = kA\Delta\rho$
 \dot{m} = mass reaction rate
k = mass transfer coefficient
A = total solid/liquid interfacial area

$\Delta\rho$ = difference in mass concentration of the diffusing species between solid surface and bulk of solution

gives the mass transfer limited reaction rate. If we assume that a dissolved zinc species is the rate-limiting diffusant, that the solution is saturated at the zinc surface, and that the zinc ion concentration vanishes in the bulk of the solution, we may calculate the reaction rate at the various flow rates. The solubility of zinc hydroxide was 0.24 gm/m³ in the 0.025% imidazole solution at pH 7.1, and by using this value, solution properties, the spherically equivalent geometric area of the 0.05-cm zinc particles, and an assumed diffusion coefficient of 10⁻⁹ m²/sec, the following reaction rates were calculated (the results are given in English units for convenience):

Flow rate, gal/hr ft ²	Reaction rate, lb/sec	
	Calcd	Obsd
1250	0.88 × 10 ⁻⁷	1.2 × 10 ⁻⁷
2500	1.2 × 10 ⁻⁷	1.5 × 10 ⁻⁷
4470	1.5 × 10 ⁻⁷	2.2 × 10 ⁻⁷

The calculated and the observed reaction rates are of the same order of magnitude, the calculated values being about 35% less than the observed values, and we may conclude that the corrosion process is well behaved in the sense of being predictable from a simple mass transfer model.

The slightly lower reaction rate at pH 5 in the imidazole-containing solution is probably not significant, but it is a change in the direction to be expected from the ionization constant of imidazole, pK = 7.12 (11). The lower the pH, the lower the concentration of the complexing unprotonated imidazole species, and the lower the concentration of the soluble zinc species that determines the mass transfer rate.

It was observed that amalgamation led to the formation of a rough surface on the zinc and it would be expected, therefore, that the pressure drop would be greater in the amalgamated zinc filter than in the unamalgamated zinc filter except at pH 7 and 8, in the absence of imidazole, where the surface roughness would be obscured by the zinc hydroxide films on the zinc surface. This was in fact the case at pH 5 where the hydroxide film is largely absent, Figure 4A and B. The analogy between mass and momentum transfer leads to the expectation of a similar increase in the corrosion rate at pH 5 upon amalgamation, but no increase was observed; amalgamation decreased the corrosion rate. A plausible explanation is that at pH 5 the rate has increased sufficiently to approach surface reaction rate control, and the mercury may have exerted its inhibiting effect on the hydrogen evolution reaction that is an integral part of the zinc corrosion process. This explanation is not entirely satisfactory since a greater rate was observed at pH 7 in the presence of amalgamation and imidazole than at pH 5 in the presence of amalgamation only, Figure 5B and D. The correct answer must

await the elucidation of the detailed mechanism of the corrosion process.

Conclusions

The study showed that the concentration of mercuric ions could be decreased from the ppm to the ppb levels in near-neutral, chloride-containing solutions by the use of a zinc filter. Typically, reaction residence times of 10 sec were needed to accomplish this degree of metal ion removal. This implies that a filter bed would have to be almost 1 ft thick to handle flows of 2500 gal/hr ft².

The adsorptive capacity of zinc appeared to be quite high. A loading of 10 wt % of mercury in the zinc did not impair the operation of the filter appreciably, and although the ultimate loading level was not determined, it is believed to be greater than 10 wt % of mercury in the zinc.

The pressure drop across the filter agreed with Ergun's correlation for packed beds when the Carman-type shape factor for Berl saddles was used for the 30/40 mesh zinc particles in the filter. The pressure drop increased with time owing to the accumulation of a zinc corrosion product in the filter. The pressure buildup was prevented by the use of imidazole to dissolve the zinc corrosion product.

The rate of corrosion of the zinc in the presence of the complexing agent agreed with Richter's equation for a liquid phase mass transfer controlled process in a packed

bed. The rate exceeded that attributable to the mercuric ion/zinc displacement reaction, and it led to an excessive zinc ion concentration in the waste stream. The latter would need to be controlled in applications of the process.

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Received for review October 23, 1973. Accepted June 20, 1974.

Convenient Method for Generation of Sulfuric Acid Aerosol

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■ A method for the generation of sulfuric acid aerosol has been devised. When a dilute solution of sulfuric acid or a solution containing sulfur is combusted under certain conditions, sulfur can be quantitatively oxidized to sulfur trioxide, which combines with moisture to form sulfuric acid aerosols. The generator consists of an atomizer burner mounted at the base of a miniature glass stack and a sampling probe mounted at the top. The burner is operated using oxygen and hydrogen. A dilute solution of H₂SO₄ is aspirated into the flame, where it decomposes to H₂O and SO₃ and possibly the elemental states. Recombination occurs to yield sulfuric acid aerosol. The aerosols, moving up the stack at a steady and controlled rate, can be collected on a suitable filter medium. Standard sulfuric acid aerosol samples can be made using this method for evaluating new analytical methods and also for inter-laboratory comparisons.

Sulfuric acid aerosol has proved to be a toxic pollutant. It has been indicted as being partly responsible for the smog disasters of London, England, and Donora, Pa., which resulted in several deaths. It is detected by odor at a concentration of 1 mg/m³, causes nose and throat irritation at 2.0 mg/m³, distinct discomfort at 3-4 mg/m³, and marked discomfort at a concentration of 6.8 mg/m³ (1).

The toxicity of sulfuric acid aerosol to man varies, apparently depending on the physical condition of the individual and other factors. Short- or long-term exposures can cause development of acute and/or chronic respiratory diseases.

The principal sources of sulfuric acid aerosols in ambient atmospheres are the combustion of fuels containing sulfur, smelting of nonferrous metals, and the refining of petroleum. Significant amounts of sulfuric acid are produced in the ambient atmosphere itself by the oxidation of sulfur dioxide to sulfur trioxide and subsequent combination of the latter with water. This oxidation process is often catalyzed by the presence of airborne metal particulates.

The common occurrence of sulfuric acid aerosols in the ambient air, and its toxic nature, necessitates the availability of reliable and specific analytical method for its determination. To test the feasibility and the reliability of any new method developed for the determination of sulfuric acid aerosols, it is essential to have standard samples and/or a reference method of analysis. Because no suitable reference method exists, the availability of suitable standards is of utmost importance. Such standards should contain known amounts of sulfuric acid aerosol and ideally would include a matrix similar to that of a typical air sample. The matrix, for example, might have preselected amounts of constituents such as soot, silica, and various metal particulates. The particle sizes of the standards

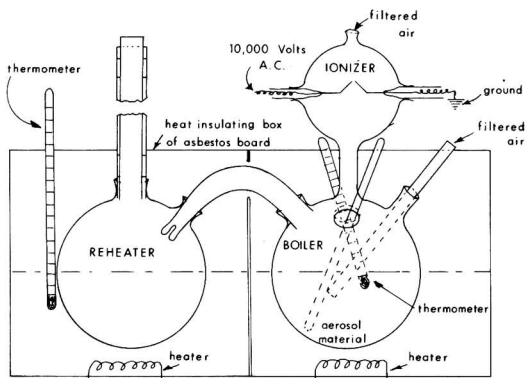


Figure 1. La Mer-Sinclair H₂SO₄ aerosol generator

should be representative of the size range found in actual samples. The method of production of the acid aerosol standards should be simple and reliable. We have developed a novel method for the generation of sulfuric acid aerosols that meets all these requirements.

Most of the methods commonly used for the generation of sulfuric acid aerosols are based on the method developed by Sinclair and La Mer (2), or some modification of their method. Their apparatus is shown in Figure 1. The aerosol is generated by placing concentrated sulfuric acid (99%) in the boiler (Figure 1) which is heated to temperatures ranging from 50-135°C. Air is bubbled through the hot acid and the ionizer simultaneously. The ionizer produces condensation nuclei, usually sodium chloride particles. The vapor formed is carried into the re-heater maintained at a higher temperature than the boiler. Thus the spray is vaporized and mixed with the nuclei to produce the aerosol. The aerosol then rises through the chimney where a sample can be withdrawn. La Mer et al. (3), in later studies, modified their method by eliminating the use of the ionizer and the bubbler, which they found unnecessary.

Coutarel and co-workers (4) have utilized a La Mer-Sinclair type of apparatus for the generation of sulfuric acid aerosol in the studies on aerosol growth. Their observations show that an inert atmosphere with constant purging of the generator is required for maintaining a constant concentration of the sulfuric acid in the boiler. Concentration, boiler temperature, and flow rates were critical factors in determining aerosol size. Their system failed to give reproducible data from day to day under presumably the same conditions.

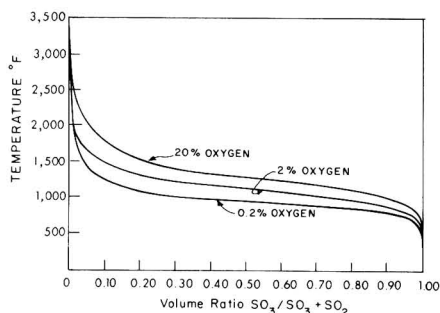


Figure 2. Equilibrium concentrations of SO₃-SO₂ at various oxygen concentrations as per reaction SO₂(g) + 1/2O₂(g) = SO₃(g). Adapted from Hougen and Watson (9)

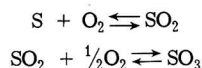
Scaringelli and Rehme (5) have reported an aerosol generator that uses fuming sulfuric acid and a condensation technique, but does not incorporate a reheater as in the La Mer-Sinclair generator.

The photooxidation of SO₂ and air in a plastic bag by irradiation with black light having a peak spectral emission at 350 nm has been reported as a method for the generation of sulfuric acid aerosol (6). Other methods of generation reported include the atomizer (7) and spinning disk generators (8).

The sulfuric acid aerosol standards made by these methods would contain only sulfuric acid, without the other normal constituents of an air sample such as soot and metal particulates. Also, it was difficult to obtain reproducible amounts of sulfuric acid using these methods owing to the difficulty in maintaining precise flow rates, controlling concentration, and establishing optimum boiler temperatures. The method we have developed overcomes these difficulties and offers a new approach for generation of sulfuric acid aerosols.

Principle

On combustion of sulfur or sulfur-bearing materials in air, the oxidation of sulfur is considered to proceed in two steps as follows:



In equilibrium conditions, the amounts of SO₂ and SO₃ produced are strongly dependent on the temperature and the relative rates of reaction. Hougen and Watson (9) have reported the equilibrium concentrations of SO₂ and SO₃ at various temperatures. As shown in Figure 2, equilibrium at ambient temperatures strongly favors SO₃ rather than the dioxide and at elevated temperatures the dioxide predominates. Again, as is evident from Figure 2, the amount of the SO₃ produced increases with increased amounts of oxygen used in the combustion.

The method we have developed for the generation of sulfuric acid aerosol is based on the reactions described above. Sulfur or sulfur-bearing compounds or solutions are continuously combusted in a controlled manner, favoring the formation of SO₃ and subsequent combination of SO₃ with H₂O to form the H₂SO₄ aerosol. The salient feature of this method is that it simulates closely the actual processes that occur in an industrial stack in the formation of sulfuric acid aerosol. The other normal constituents of an airborne particulate sample such as soot, silica, and metal particulates can also be generated under the same conditions (10). Thus, using this method one can produce composite airborne particulate samples, containing known amounts of sulfuric acid aerosol, metal oxide particulates, silica, and soot, in desired ratios of their concentrations.

Construction of Generator

The aerosol generator is based on the design of the metal particulate generator developed by Dharmarajan and West (10). The generator consists of a total consumption atomizer burner (like the ones used in commercial flame photometers) mounted at the base of miniature Pyrex glass stack, open at both ends. A sampling probe also made of Pyrex glass, is inserted from the top of the stack. The rim of the sampling probe is ground to a sharp edge to minimize the deflection of the aerosol. A filter holder made of Teflon is connected to the sampling probe by means of Tygon tubing, which, in turn, is connected to a wet test meter and a vacuum pump. The schematic diagram of the aerosol generator is given in Figure 3.

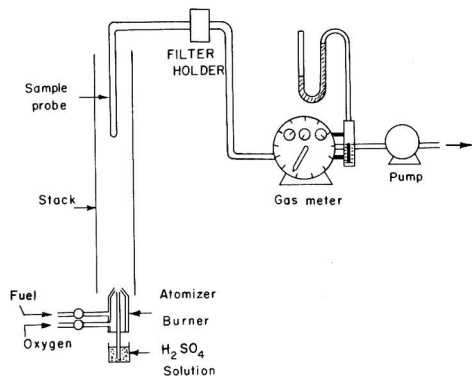


Figure 3. Sulfuric acid aerosol generator

Operation of Generator

The atomizer burner is operated with acetylene or hydrogen as the fuel and oxygen as the oxidant. Acetylene is used when soot is desired in the sample collected. A solution containing dissolved sulfur or even a dilute solution of H_2SO_4 is aspirated into the flame at a steady rate. The aspirated solution is atomized in the burner, and when it reaches the flame, the solvent evaporates and in the case of sulfuric acid decomposition it separates into H_2O , SO_3 and possibly SO_2 , S, O, and H. When the sulfur atoms leave the flame, they recombine according to the reaction discussed previously. The reaction conditions in the stack are such that it favors the formation of sulfur trioxide rather than SO_2 . Also, the combustion of hydrogen or acetylene with oxygen produces water, which combines with SO_3 to produce the H_2SO_4 aerosol. The aerosol so formed moves up the stack at a steady rate. The rate of formation of the aerosol can be precisely controlled by regulating the aspiration rate, which, in turn, is controlled by the flow rates of oxygen and fuel. Thus, once a steady state is reached in the stack, the acid aerosol moves up the stack with a constant velocity.

Experimental

Apparatus and Materials. Atomizer burner: Beckman Flame Photometer Burner assembly with oxygen/fuel regulators; Pyrex stack: length = 60 in., i.d. = $3\frac{3}{4}$ in.; Pyrex sampling probe: i.d. = $\frac{5}{16}$ in.; Teflon filter holder: made by chemistry department workshop, LSU, to hold 47-mm filter; pump: Model 2300, Gelman Instrument Co., Ann Arbor, Mich.; wet-test meter: E. H. Sargent and Co., Chicago, Ill.; Tygon tubing: i.d. = $\frac{1}{4}$ in. and i.d. = $\frac{3}{8}$ in.; oxygen, acetylene, and hydrogen tanks; Leitz Ortholux Research Microscope; filters: MF-Millipore (HA), 0.45μ , 47-mm diameter, Whatman No. 41, Mitex (Teflon) 5.0μ , and graphite filters from Spectrogram Corp., North Haven, Conn.; Beckman DB Spectrophotometer.

All the reagents used were of analytical reagent grade: Sulfuric acid, 0.0200N standard solution, Kem-Tech Laboratories, Inc., Baton Rouge, La.; bromophenol blue, Matheson Coleman & Bell 0.05% water solution; chloranilic acid, Fisher Scientific Corp.; barium chloranilate, prepared by precipitation of an aqueous solution of chloranilic acid upon addition of $BaCl_2 \cdot 2H_2O$. Enough $BaCl_2 \cdot 2H_2O$ is added until the dark purple color due to chloranilate ion disappears indicating completion of reaction with chloranilic acid. A dark brown precipitate was noted during the process. The precipitate was collected by vacuum filtration and then washed with 80% isopropanol for 1 hr in a beaker, with the aid of a magnetic stirrer and hot

plate. Temperature was maintained at approximately $75^\circ C$. The solution was filtered and the barium chloranilate was washed with hot isopropanol. The purified crystals were then dried under vacuum for 16 hr.

Procedure

The atomizer burner was operated with either acetylene and hydrogen as the fuel and oxygen as the oxidant. Fuel flow was regulated at 1.0 psi and the oxidant at 12.5 psi. The sampling probe was located in the center of the stack, 48 in. above the top of the burner. The system was allowed to equilibrate by aspirating the feed solution for about 5 min before samples were collected. A steady state was thus attained and a constant temperature of $114^\circ C$ was obtained at the sampling site.

Samples were collected on various filter media to include such filters as paper, glass fiber, Millipore, graphite, and Teflon. The sample on filter paper was taken using a sequential tape sampler (Gelman Instrument Co.) and for Millipore, graphite, and Teflon filters, a special filter holder was made of Teflon. The sampling times were measured accurately with a stopwatch. A sampling rate of 0.43 CF/min was maintained throughout the study. Sample blanks were collected immediately after each sample run by aspirating the appropriate solvent.

The above experimental conditions were maintained throughout the studies described below unless indicated otherwise.

The samples collected were analyzed for H_2SO_4 content by two different methods. The barium chloranilate method (11) which measures the sulfate concentration and the bromophenol blue method developed recently in this laboratory by Chiang and West (12) which measures the proton concentration. The two procedures are described below.

Barium Chloranilate Method. The filter containing the H_2SO_4 aerosol was placed in a 150-ml beaker and washed four or five times with small amounts of deionized water. The washings were added to a 10-ml volumetric flask containing 8 ml of isopropanol and diluted to the mark with deionized water. The contents of the flask were transferred to polyethylene bottles containing 25 mg barium chloranilate and shaken mechanically for 30 min. After shaking, the solutions were decanted into centrifuge tubes and centrifuged for 2 min. The absorbance of the decantate containing the chloranilate ions displaced by the SO_4^{2-} was measured at 310 nm for 0-10 ppm range or

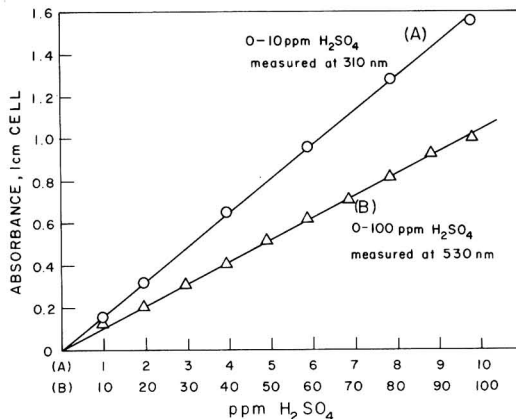


Figure 4. Calibration curves—barium chloranilate method
(A) 0-10 ppm range of H_2SO_4 measured at 310 nm
(B) 0-100 ppm range of H_2SO_4 measured at 530 nm

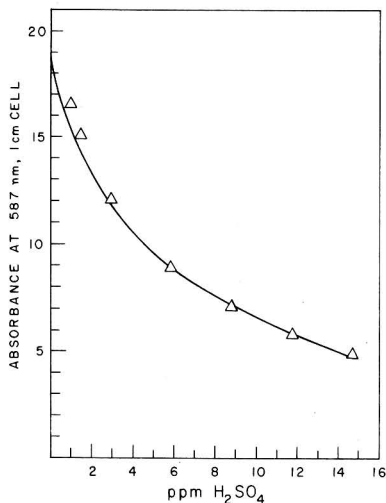


Figure 5. Calibration curve—bromophenol blue indicator method

at 530 nm for the 10–100 ppm range. Calibration curves were made for both the ranges by taking appropriate amounts of standard H₂SO₄ and following the above procedure. Calibration graphs are shown in Figure 4.

Bromophenol Blue Indicator Method. This method is based on the degree of the shift due to protons of the equilibrium concentration of the salt to acid forms of the indicator. The shift in the equilibrium concentrations of the indicator was measured spectrophotometrically by reading the absorbance at 587 nm.

The filter containing the H₂SO₄ aerosol was placed in a 150-ml beaker and washed five times with deionized water. The washings were transferred to a 50-ml volumetric flask containing 3 ml of 0.05% bromophenol blue solution and made up to the mark with deionized water. The absorbance of this solution was measured at 587 nm. A calibration curve was prepared by taking appropriate amounts of standard H₂SO₄. The calibration curve is shown in Figure 5. In the samples analyzed by this method, dilutions were made to appropriate volumes depending upon the amount of acid collected in order that absorbance readings would fall on the calibration curve.

Results and Discussion

Initially, trial experiments were performed to confirm the production of H₂SO₄ aerosol and to determine whether some other compounds of sulfur might also be produced. The most likely sulfur compound to be produced would be sulfur dioxide. The possible production of SO₂ was tested by the West-Gaeke procedure (13). A scrubber containing sodium tetrachloromercurate(II) solution was connected to the sampling probe (in the place of the filter holder) in the sampling train. A saturated solution of sulfur in isopropanol and an aqueous H₂SO₄ solution (980 ppm) were aspirated into an air-acetylene flame. Samples were collected for different lengths of time up to 1 hr. The analysis of the tetrachloromercurate(II) scrubbing solution for SO₂ by the West-Gaeke method failed to indicate the presence of even traces of SO₂. Hence, it was concluded that all the sulfur was being converted to SO₃ under the established experimental conditions.

The feasibility of generation of sulfuric acid aerosol was studied by aspirating a solution of sulfur in isopropanol into an air-acetylene flame. Samples were collected in a scrubber containing dilute NaOH and the resultant solu-

tion was analyzed for sulfate content by a pyrolytic method developed by Maddalone and West (14). The analysis confirmed the presence of substantial amounts of sulfates. Reproducible generation of sulfuric acid aerosol was found difficult, when aspirating a sulfur solution, owing to problems of nonuniform aspiration. Sulfur deposits were formed in the burner capillary and the flame was unsteady and flickering. To overcome these problems dilute solution of sulfuric acid itself was aspirated into the flame to determine whether sulfuric acid aerosol was being produced. Interestingly enough, the combustion of sulfuric acid solution in the flame did produce sulfuric acid aerosol and the aspiration was smooth, with no problems of burner clogging or unstable flames. In all the further experiments, therefore, dilute solutions of sulfuric acid were used as feed.

To confirm that H₂SO₄ aerosol was being generated, the following experiments were performed: A 980-μg/ml solution of H₂SO₄ was aspirated into an oxyhydrogen flame and two sets of samples were collected for 2, 5, 10, 15, and 20 min using Millipore filters. Blank samples were also collected concurrently by aspirating deionized water under the same conditions. One set of the samples was analyzed using the barium chloranilate method and the second set was analyzed using the bromophenol blue method. The results are shown in Figure 6. From the figure it is clear the values for H₂SO₄ obtained by the two completely independent methods agree well. The barium chloranilate method determines the amount of H₂SO₄ by measuring the amount of SO₄²⁻, whereas the bromophenol blue method, on the other hand, measures the amount of H⁺ liberated. The close agreement between these two methods conclusively proves that the species generated is H₂SO₄ aerosol. The linear and proportional increment of the amount of H₂SO₄ collected with time, as shown in Figure 6, also indicates the reliability and reproducibility of this method of generation.

The precision of generating standard samples was studied by collecting seven samples, each of 8-min duration, under the same conditions as described above. Samples and blanks were analyzed using the bromophenol blue method. A 4.2% coefficient of variation was obtained. The results are tabulated in Table I.

The efficiency of four different filters for the collection of the aerosol was tested by aspirating a 980-ppm H₂SO₄ solution into an oxyhydrogen flame. Samples were collected for the same length of time. Because the pressure drop across different filters varies, a rotameter was incorporat-

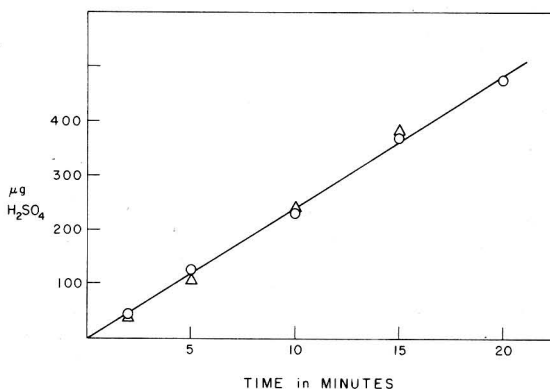


Figure 6. Amount of H₂SO₄ generated as function of time
 Δ. Barium chloranilate method
 ○. Bromophenol blue method

Table I. Reproducibility of H₂SO₄ Aerosol Samples

Sample	H ₂ SO ₄ , μg
1	205
2	193
3	213
4	213
5	195
6	205
7	195
MEAN 203 ± 4.2% ^a	

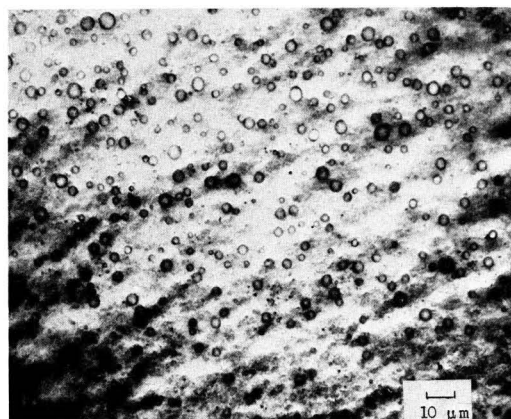
^a Coefficient of variation.

Table II. Comparison of Filter Efficiency

Filter	Barium chloranilate method, μg of H ₂ SO ₄	Bromophenol blue method, μg of H ₂ SO ₄
MF-Millipore (HA)	325	325
Whatman No. 41	300	295
Mitex (Teflon)	187	172
Graphite	257	252

ed before the filter, and the flow rates were adjusted to the same value using a needle valve. Once the flow rate was adjusted, the rotameter was removed and the sample collected for the time desired. Thus, the volume of air sampled in each case was equalized. The samples were analyzed by both the barium chloranilate and the bromophenol blue methods. The results are given in Table II. Of the four different filter mediums tested, viz., Millipore, Whatman 41, Teflon, and graphite, Millipore was found to have the best and Teflon had the least efficiency. The excellent correlation between the values obtained by these two different methods gives added proof to the fact that the species being generated was exclusively sulfuric acid, free from other acidic or sulfate compounds.

Preliminary investigations indicate that the size of the sulfuric acid aerosols generated falls in the respirable range—i.e., 0.1–5 μ. The size was determined by collecting the sulfuric acid aerosol on Fluoropore filters and observing under a light microscope (Leitz Ortholux Research Microscope). A typical aerosol sample thus collected is shown in Figure 7. The Teflon filters were used because the other filters such as Whatman 41, Millipore, etc., were opaque, which made it difficult to get suitable pictures of

**Figure 7.** Typical H₂SO₄ aerosol sample

the aerosols. The size distribution of a sample collected on Teflon filter for 1.5 min is given in Table III. The numbers in Table III may be somewhat misleading because of the coalescence of the aerosol during the process of collection. The average size of the aerosols generated is probably less than the 2.5 μm indicated in Table III. The coalescence is dramatically indicated in Figure 8, which shows samples collected for 3, 5, and 7 min and photographs of the aerosol taken at different locations on the filter. The size of the aerosols generated is important, especially for toxicologic studies, and there is need for further studies in this area. However, this paper is primarily directed toward analytical chemists who are in need of standard sulfuric acid reference material for testing new methods developed and for interlaboratory and intralaboratory comparisons of analytical techniques.

Conclusion

A method has been developed for the production of standard H₂SO₄ aerosol, using a generator which is simple, reliable, and versatile. The aerosol is generated in a manner similar to its production in the environment i.e., combustion of sulfur-containing compounds. The aerosol can be generated along with soot, if desired, by using an oxyacetylene flame. The generator has also the versatility of producing metal particulates simultaneously with H₂SO₄ aerosol.

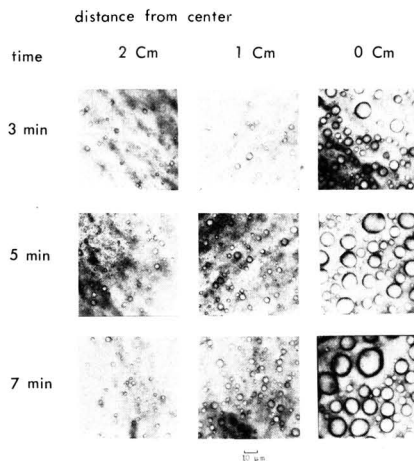
Millipore filters are recommended as the filter of choice to collect the aerosol. Filter paper is also satisfactory.

Table III. Size Distribution of Typical Aerosol H₂SO₄ Sample

Size range in μm ^a	No. of aerosols	% distribution
0.0–1.0	14	3.8
1.0–2.0	113	31.3
2.0–3.0	126	34.9
3.0–4.0	94	26.0
4.0–5.0	12	3.3
5.0–6.0	2	0.6
Total 361		

2.5 μm average size

^a Exclusive of second number.

**Figure 8.** Coalescence of H₂SO₄ aerosol

This method of generation of H₂SO₄ aerosol has the unique capability of preparing realistic standard particulate samples containing known amounts of H₂SO₄, together with controlled amounts of soot and/or metal oxides. This can be very valuable for interlaboratory and intralaboratory comparison of analytical techniques and for verifying new analytical methods developed for the determination of H₂SO₄ aerosol. It should also be helpful in simulating complex atmospheres containing soot, metal particulates, acid aerosols, and gaseous pollutants, as test atmospheres for use in toxicological, industrial hygiene, and air pollution studies.

Acknowledgment

The authors wish to thank John P. Jendrzewski and Ray F. Maddalone for their assistance in photographing the aerosols.

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Received for review December 13, 1973. Accepted June 24, 1974. Work supported in part by the NSF, RANN GI-3524XI project and the NSF Foundation Grant No. GP 18081.

Composition of Organic Constituents in Breathable Airborne Particulate Matter Near a Highway

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■ Particulate matter (PM) was collected in parallel experiments by Hi-Vol and Andersen samplers over periods of 54–96 hr along a highway complex in New York City. Atmospheric concentrations of 89–125 $\mu\text{g}/\text{m}^3$ were obtained for the Hi-Vol sampler; the Andersen sampler yielded much lower values. The breathable particles (Andersen samples containing particle size range of 0.43–7.0 μm) and total particulate samples (Hi-Vol samples) were extracted with benzene and separated chromatographically on silica gel. Empirical formulas calculated from the experimental data are similar to a formula obtained by Sawicki et al. Percentages of oxygen in PM from both sample collectors are about equal for parallel experiments, but with higher nitrogen content in Andersen samples. The oxygen, carbonyl, nitrogen, and double bond content greatly favor the 2-propanol Andersen fractions. Spectroscopic evidence shows the presence of aldehydes, ketones, acids, hydroxylic groups and possibly oximes, organic nitrogen substances, and aza heterocyclic compounds in an oxidized polymerized hydrocarbon matrix in PM arising from a pyrosynthetic combustion process in cars. From a log normal distribution of total particulate matter with an MMD of 0.43 μm , the breathable (Andersen) samples represent 55, 50, and 28% of the particulate matter deposited in the NP, TB, and P lung compartments, respectively. The 2-propanol fraction of the Andersen samples appears to pose a potential threat to health considering the possibility of extracting the polar organic contaminants in a number of different clearance paths in the body because acids and oxygenated neutral organic matter from air particulate matter have been shown to have tumor-promoting properties on initiated skin; some aza heterocyclic substances found in particulate matter are carcinogenic, and Zikria suggested that aldehydes were the causative agent in smoke poisoning in experiments with dogs.

Recently Cukor et al. (1) categorized chemically, benzene-extracted organic matter derived from airborne particulate matter collected near a New York City highway complex. However, no similar study has been made of the extracted organic matter in the breathable fraction of airborne particulate matter. It indeed would be informative from the viewpoint of environmental health to realize the variation of distribution of organic substances as a function of aerodynamic size, particularly of the breathable size range as compared to the total collectable airborne particulate matter (2). The importance of oxygenated organic substances acting as cocarcinogens and carcinogens has been given and their possible presence in particulate matter was particularly observed (1, 3, 4).

Primary standards for airborne particulate matter have been promulgated recently (5, 6). The use of the Hi-Vol sampler appears to be adequate and accurate (7–11) for the determination of airborne concentrations of total suspended particulate matter. However, an expansion of the standards to include other characteristics important to community health such as particle size distribution and chemical composition of the particles as well as chemical content and concentration as a function of aerodynamic size should be considered (12–16).

A definition of breathable particulate matter includes particles with sizes such that they are captured and reside in the various compartments of the respiratory system—i.e., the nasopharyngeal (NP), the tracheobronchial (TB), and the pulmonary (P). A further consideration is the dependence of chemical content on particle size. For exam-

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ple, the variation of inorganic chemical content of particulate matter as a function of particle size was shown to exist by a number of investigators (12-15). A variety of metals, such as lead, zinc, iron, copper, nickel (12-14), and other materials, such as sulfate ion (15), show higher concentration in a given range of particle sizes. In addition, the clearance mechanisms resulting in removal of these particles from the various compartments of the respiratory system via the circulatory and lymphatic systems and the alimentary canal widen internal bodily contact of the particles and/or their extractable components (17). Thus, our objective was to collect and analyze breathable particulate matter for their organic chemical content using a suitable collecting device.

An Andersen sampler was chosen to collect breathable particles (18). With this device as calibrated by the manufacturer (19, 20), the particles collected on stages 2 through 7 representing aerodynamic sizes from 0.43 to 7.0 μm were purported to be deposited in the three compartments of the lungs (19).

Parallel collections, in time, of particulate matter by Hi-Vol and Andersen samplers, were made at a sampling station near a large highway intersection adjacent to the Throgs Neck Bridge in New York City. Several Andersen stages representing the breathable zone were composited and weighed. The organic substances from Andersen samples and the benzene-extracted organic substances from Hi-Vol samples were resolved chromatographically on silica gel and the fractions were weighed and analyzed for elemental composition and infrared spectroscopic characteristics (1). Distribution of organic fractions in total particles (Hi-Vol samples) and the breathable particles (Andersen samples) was then determined.

Experimental

Sample Collection. The Andersen sampler, Model 21-000 (19), containing stages 0-7, with a 1-mil thick polypropylene circle on each stage was conditioned at a controlled temperature and humidity for 24 hr, usually at 25°C and 50% RH (relative humidity). After 24 hr the polypropylene circles on each stage were weighed and replaced on the stages; the sampler was assembled and collection commenced for periods ranging from 54-96 hr. A sampling rate of 1 std ft³/min (scfm) was used. At the end of the sampling period, the Andersen sampler was conditioned as described and the polypropylene circles containing the collected particulates for the respective stages were reweighed. In this manner a weight of particulate matter for such stage was obtained. Two Andersen samplers were used for each experiment.

Total particulate matter was collected in a Staplex Hi-Vol sampler housed in a proper shelter allowing sufficient air access, yet protecting the glass fiber filter (Gelman Type A, 8 × 10 in., flash fired) from rain and light. One filter was used for each Hi-Vol experiment, whether the sampling time was 54, 72, or 96 hr. No change in volumetric flow rate (50 cfm) was observed during these time periods and thus a change of filter was deemed unnecessary and analytically inconvenient [see Cukor et al. (1) for other details].

Extraction and Fractionation of Organic Substances in Particulate Matter. The particulate matter was vacuumed from polypropylene circles representing stages 2 through 7 (breathable particulates) and composited. The vacuuming device consisted of an eye dropper 4 cm long containing a small plug of preweighed quartz wool. The vacuum was applied at the wide end and the tip was used to pass along the surface of the circle in order to remove the particulate matter. Once the particles were deposited

on the quartz wool plug, it was removed and reweighed to determine the mass of particulates which had been removed from the stages and deposited on the plug.

The quartz wool plug containing the particulates was placed on top of a 4-cm height of silica gel (Biosil A 100-200 mesh, Bio Rad Lab, Richmond, Calif.) housed in an eyedropper. The chromatographic separation of the organic constituents was then commenced. The following spectral grade solvents were used in the order given: 5% benzene in hexane (hexane-benzene), chloroform, 2-propanol, methanol, acetone, and hot acetone.

The chromatographic procedure was as follows: 1½ ml of the solvent was passed through the column. It was collected and passed through again. This was continued until 10 passes of the solvent had been made through the column. During this procedure, the migration of the band down the column and its elution were observed. Finally 0.5 ml of solvent was used to wash down the column. During this procedure some solvent was lost due to holdup on the column, but the final volume obtained was usually 1 ml. This procedure allows for use of a minimal volume of solvent keeping any blank contribution from the solvent at a low level relative to the sample. However, the critical separation process, solvent elution, is not disturbed by this recycling technique. The solvent eluate was then evaporated in a tared beaker and the weight of the respective fraction obtained. The residue was treated with chloroform (in which all fractions were soluble or suspendible) and deposited on a sodium chloride or cesium bromide plate for infrared examination. The evaporation was carried out by allowing the solvent to evaporate naturally at room temperature after which it was subjected to vacuum to remove the last traces of solvent. The plate was placed in the infrared spectrophotometer (Perkin-Elmer Model 621), and a mask was utilized to close down the beam so that it was no larger than the circular film of sample. The spectrum was obtained at slow speed (16 min, full spectrum) and sometimes with scale expansion factors of 2X and 5X. This was necessary to obtain details of small peaks, particularly for fractions from Andersen samples [see also Cukor et al. (1) 1972]. The residue was removed from the salt plate with chloroform, recovered, and subjected to elemental analysis. Solvent blanks were carried through the chromatographic and ir procedure and were found to contain negligible amounts of C-H absorbing substances compared to sample absorptions.

The extraction, fractionation, and analysis of the total organic matter in particles collected on Gelman glass fiber filters in the Hi-Vol sampler was accomplished by the procedure given in a recent report (1). The 8-hr benzene extraction was carried out on the glass fiber filters immediately upon removal from the Hi-Vol sampler to eliminate possible loss of volatile materials from the filters during storage. Solvent blanks carried through the total procedure showed relatively small amounts of C-H absorbing materials when they were compared to the sample absorptions.

Since a number of samples and fractions were isolated and analyzed, the following system was utilized to identify the fractions: Experiments or samples 1, 2, 3, and 4, both sampling techniques—Andersen = A and Hi-Vol with Gelman filters = G—and all fractions, hexane-benzene = 1; chloroform = 2; 2-propanol = 3; methanol = 4; acetone = 5; and hot acetone = 6. Therefore, 2A3 represents Experiment 2, Andersen sample, 2-propanol fraction.

Carbon, hydrogen, and nitrogen analyses were obtained by use of a Perkin-Elmer Model 240 Analyzer. The oxygen analyses were obtained through neutron activation analysis utilizing a neutron generator, TMC Model 211.

Table I. Percent Weight Distribution on Andersen Sampler Stages^a

Stages	Size range, μm^b	Expt 1, ^c	Expt 2		Expt 3		Expt 4		Av % values	Av particle diam
			I	II	I	II	I	II		
7	0.43-0.65	18.2	15.8	21.8	27.2	16.8	18.9	12.6	18.8	0.54
6	0.65-1.1	15.3	11.8	11.2	8.9	13.0	6.7	11.9	11.3	0.88
5	1.1-2.1	7.6	1.91	13.6	18.1	16.2	16.1	17.0	15.4	1.6
4	2.1-3.3	11.8	12.0	11.2	11.9	10.9	4.9	13.5	10.9	2.7
3	3.3-4.7	13.6	10.5	12.6	6.7	8.7	10.7	12.6	10.8	4.0
2	4.7-7	13.6	11.5	11.5	10.6	11.1	16.9	8.0	8.7	5.9
1	7-11	10.1	9.5	7.3	8.6	6.5	9.7	8.9	12.4	9.0
0	>11	9.8	9.8	10.8	8.0	16.8	16.1	15.5	12.4	

^a Two samplers, I and II, were used in each experiment and dates carried out are given in Table III, except for Expt 1-Nov. 5-8, 1971. ^b Flesch et al. (20) and Andersen 2000 Inc. (19). ^c The value for Expt 1, II was not included because of a cracked glass Andersen plate.

Results and Discussion

In Table I the percent weight distributions on Andersen sampler stages for the various experiments are given. The experimental recovery, by vacuuming, of particulate matter from Andersen stages was about 89%. The particulate matter thus collected on a piece of quartz wool was separated on a silica gel column. The fractions separated were analyzed for their elemental composition. In the elemental analyses, the sum of the % recoveries of the elements C, H, N, and O varied from 82.0-101.7%. These include eight analyses; 4 above 97%, 6 above 93%, and 2 at 87.5 and 82.0%. Other analyses did not include oxygen determination and the amount of this element was estimated from the difference between 100% and the total percent recovery of C, H, and N (see Table II, Note a).

The legitimacy of comparing the organic chemical distribution for Hi-Vol and Andersen samples is based on the complete extraction of organic compounds from Hi-Vol samples using benzene. Methodology concerning the Andersen samples ensures removal of organic substances, since the particulate sample is placed directly on the chromatographic column. Recently one of the authors (21) has shown that an 8-hr extraction with pure benzene will remove all the organic matter from Hi-Vol samples. The

samples used for that investigation were collected during the same time period of the presently reported parallel collection experiments. The procedure consisted of a sequential Soxhlet extraction of Gelman filters with benzene, chloroform, 2-propanol, methanol, and acetone. After evaporation of each solvent, the residue was examined by ir. No C-H absorption was found in the residues from solvents following benzene although inorganic substances were detected. Thus, for these samples, benzene Soxhlet extraction appears to remove the organic substances present. However, investigators have experienced incomplete extraction of some compounds using benzene (22). Since the organic content of particulate samples are bound to vary for different locations and times, the efficiency of extraction must be established by each investigator vis-a-vis his samples.

Recently Lee et al. (8) showed a correlation of +0.940 when comparing the airborne particulate concentrations determined in parallel collection experiments using a Hi-Vol sampler and a NASN cascade impactor. However, the differences between atmospheric concentrations as derived from Andersen and Hi-Vol collection regimes determined here are quite large, amounting to 200 to 500% (Table III). Some facts which may explain this discrepancy should be examined.

Table II. Comparison of Chemical Characteristics of Organic Fractions in Experiments 2, 3, and 4

Fraction	Hi-Vol (total particulates)				Andersen (breathable particulates)		
	Empirical formula		Double bonds ^b	Infrared C=O/CH	Empirical formula ^a	Double bonds ^b	Infrared C=O/CH
Experiment 2							
Hexane-benzene	C ₃₂ H _{62.8} N _{0.2} O _{0.3} ^a		1-2	0.00	C ₃₂ H ₃₀ N _{5.7}	13-14	0.00
Chloroform	C ₃₂ H _{48.8} N _{0.5} O _{3.6} ^a		4-5	0.41	C ₃₂ H _{35.9} N _{0.5}	15	0.10
2-Propanol	C ₃₂ H _{45.5} N ₁ O _{8.4} ^a		4	1.05	C ₃₂ H _{38.4} N _{1.9} O _{8.4}	5	0.74
Methanol	C ₃₂ H _{48.3} N _{3.6} O _{6.6} ^a		1-2	1.37	c		
Acetone	C ₃₂ H _{38.2} N _{2.0} O _{8.5} ^a		8	0.72	c		
Hot acetone	d			0.78	c		
Experiment 3							
Hexane-benzene	C ₃₂ H ₆₀ N _{0.3} O _{0.1} ^a		1-2	0.00	C ₃₂ H _{48.8} N _{5.3}	8-9	0.00
Chloroform	C ₃₂ H ₅₀ N _{0.2} O _{4.5} ^a		3	0.50	d		0.27
2-Propanol	C ₃₂ H _{48.1} N _{1.1} O _{8.8} ^a		3	0.90	C ₃₂ H _{34.5} N _{1.5} O _{3.2}	12-13	0.63
Methanol	C ₃₂ H ₄₃ N _{2.5} O _{14.5}		c	1.11			
Acetone	C ₃₂ H _{39.2} N _{2.9} O _{5.5}		8	0.73	c		
Hot acetone	d				c		
Experiment 4							
Hexane-benzene	C ₃₂ H ₅₇ N _{0.6}		4-5	0.00	C ₃₂ H _{51.5} N _{10.5}	7	0.00
Chloroform	C ₃₂ H _{58.5} N _{0.6} O _{4.7}		1-2	0.37	C ₃₂ H _{46.3} N _{8.2} O _{1.8}	8	0.61
2-Propanol	C ₃₂ H _{42.4} N _{1.1} O _{10.4}		2	0.90	C ₃₂ H _{43.7} N _{6.2} O _{7.1}	4	0.70
Methanol	C ₃₂ H _{42.9} N _{1.8} O _{11.3}		1-2	0.95	c		
Acetone	C ₃₂ H ₃₄ N _{2.9} O _{8.3}		12-13	0.50	c		
Hot acetone	C ₃₂ H _{32.4} N _{0.1} O _{10.8}		5-6	0.39	c		

^a Oxygen analyses performed; on all other samples oxygen content estimated by difference. ^b Number of double bonds = $[66 - (\#H + 2 \times \#O)]/2$. ^c No fraction detected. ^d Insufficient sample for analysis. ^e Overcorrection leads to a negative result.

Table III. Atmospheric Distribution of Particulate Matter and Organic Fractions

Variable	Experiments ^a					
	2 (11/16-19/'71)		3 (12/20-22/'71)		4 (2/21-25/'72)	
	Hi-Vol (total)	Andersen (breathable)	Hi-Vol (total)	Andersen (breathable)	Hi-Vol (total)	Andersen (breathable)
Collection time, hr	72	72	54	54	96	96
Particulate matter, $\mu\text{g}/\text{m}^3$	96.6 ^b	32.6 ^c	124.6 ^b	20.9 ^c	89.1 ^b	16.5 ^c
	Fraction, $\mu\text{g}/\text{m}_3$					
Hexane-benzene	5.40	0.25	7.35	0.24	1.16	0.13
Chloroform	3.09	0.37	3.12	0.21	1.70	0.35
2-Propanol	3.57	1.65	3.24	1.01	1.96	1.12
Methanol	0.55	...	0.20	...	0.45	...
Acetone	0.20	...	0.27	...	0.18	...
Hot acetone	0.05	0.36	...
Total organic matter, $\mu\text{g}/\text{m}^3$	12.86 ^b	2.27 ^c	14.18 ^b	1.46 ^c	5.81 ^b	1.60 ^c

^a Experiment 1 was not carried out quantitatively. ^b These values are based on total particulate sample weights of 336.8, 295.4, and 365.5 mg, corresponding to extracted organic sample weights of 45.3, 34.0, and 29.3 mg, for samples 2, 3, and 4, respectively. ^c These values are based on breathable particulate sample weights of 7.980, 5.825, and 5.370 mg, corresponding to extracted organic sample weights of 0.550, 0.240, and 0.525 mg, for samples 2, 3, and 4, respectively.

The Andersen sampler in this study was limited to the collection of particles which have an aerodynamic diameter no smaller than 0.43 μm (Table I). Since no downstream filter was placed after the seventh stage, none of the smaller particles were collected. From an examination of data from six American cities cited by Lee and Goranson (9) and Lee (11) and highway data (11), a MMD of 0.43 μm is a reasonable value for a log normal distribution of airborne particulate matter. Therefore the Hi-Vol particulate concentration should be about 100% larger than a parallel Andersen experiment.

Several other effects have been given for lower collection efficiency by a cascade impactor. Wall losses are attributed by Lee et al. (8) to the discrepancy between airborne particulate concentrations determined in parallel collection experiments by a Hi-Vol sampler and a cascade impactor. However Lundgren (23) demonstrates that wall losses increase with increasing particle diameter and are rather small—i.e., 0.3% for 1-2 μm , 0.7% for 3.0 μm , and 6.5% for 5.2 μm . Also the use of polypropylene collection surfaces, although convenient may provide a surface charge which could interact with a charged particle impinging on the surface causing low collection efficiencies. A full accounting of the discrepancy in the collection abilities of these two devices can't be given although a 100% error is explainable.

Since only a portion of the breathable particles have been collected by the Andersen sampler a meaningful quantitative relationship must be developed relating the sample collected to the breathable particles found in the respiratory system. This is carried out as follows: The data given in Table I were used to obtain a log normal curve by relating the average weight (for seven experiments) collected on each stage to the average size for that stage. (The average weight for particulate matter on each stage is given in % or grams of particle on a specific stage/100 g of particulate sample.) The log normal curve (A, Figure 1) provided smoothed data relating the average of each size range to the cumulative % weight smaller than that average size. This first log normal curve A, had the following characteristics: MMD = 2.0 μm , 31.5% \leq 1.0 μm (Figure 1). This result is not characteristic of particulate data obtained from American cities and near high-

ways (9,11). Therefore a composite log normal curve was constructed, assuming the MMD of the particle spectrum at the sampling station was 0.43 μm and utilizing the experimental data and its log normal curve (A, Figure 1). The Andersen samples were assumed to represent 50% of the particle spectrum—i.e., particles \geq 0.43 μm . The composite log normal curve (B, Figure 1) resulted which is similar to the average for six American cities and highway data. The characteristics of particulate data for this composite curve are as follows:

$$\text{MMD} = 0.43 \mu\text{m (as chosen); } 66\% \leq 1.0 \mu\text{m and } 77\% \leq 2.0 \mu\text{m}$$

With the composite log normal curve (B, Figure 1), the particulate sample collected in the Andersen sampler can be related to the particulate matter deposited in the various lung compartments. Because the particulate matter collected in the Andersen sampler in this investigation doesn't include the particle sizes $<0.43 \mu\text{m}$, a meaningful comparison of the experimental and true particle spectrum was sought. A simple integration was carried out using the data from the composite log normal curve (B, Figure 1) and the percent deposition vs. size data for various lung compartments (17). The total amount of material deposited in each compartment; nasopharynx, NP; trachea and bronchi, TB, and pulmonary, P, was thus calculated for the total composite log normal curve and compared to that portion attributable to the experimental data which included the breathable particles, Andersen stages 2-7, representing particle sizes 0.43-7.0 μm . The experimental data account for the following percentages of particulate matter deposited in lung compartments: 55% NP, 50% TB, and 28% P. These values represent 16.5, 8.0, and 8.6 g/100 g, respectively, of deposited particulate matter.

The atmospheric distribution of fractions and chemical characteristics of Andersen and Hi-Vol samples can be compared. Particulate matter from Andersen stages 2-7 representing particle sizes 0.43-7.0 μm were composited and analyzed. However, since such a large discrepancy existed between the atmospheric concentrations as determined by parallel Hi-Vol and Andersen collection experiments, a suitable mathematical means of comparing distributions of analytical characteristics in the various chro-

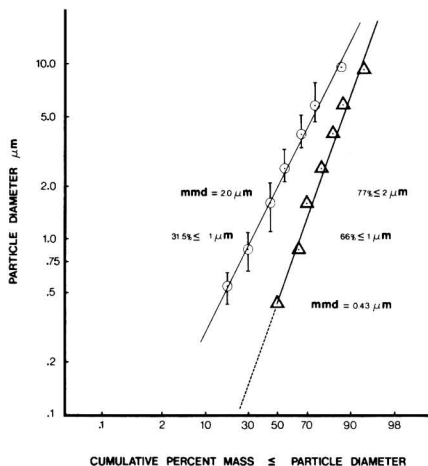


Figure 1. Log normal distributions of Andersen samples. O, average Bayside values (Table I); Δ , composite curve.

matographic fractions of the samples was required. Therefore analytical values for % weight distributions of the total organic matter, TOM, and organic fractions in particulate matter, PM, were determined. Double bond, oxygen, carbonyl, and nitrogen content of Andersen and Hi-Vol samples were used to determine the % distribution of these variables for each chromatographic fraction as a function of weight of PM (Equation 1) and as a function of the weight of TOM (Equation 2).

The qualitative and quantitative aspects of the organic fractions resolved from Andersen and Hi-Vol particulate samples as indicated by the empirical formulas and ir carbonyl ratios (Table II and typical spectra in Figures 2 and 3) can be used to determine the carbonyl, nitrogen, and oxygen distribution in particulate matter and total organic matter. These values for % distribution of the chemical characteristics for the Hi-Vol and Andersen fractions for parallel experiments can be compared to determine differences and trends in the samples which can be quite important in determining the character and giving an estimate of the environmental human insult due to particulate samples.

The concentration of the fractions in the atmosphere (Table III) indicates different trends when comparing each sample collection technique. This can be observed in Table IV where the weight percent distribution of the organic fractions of the particulate matter is compared for each collection method. The % TOM in particulate matter varies for the two collection techniques although they are reasonably close to the range found in nationwide particulate samples, about 4-14% (24, 25). In two cases, experiments 2 and 3, the Hi-Vol samples showed a considerably higher total organic content than the respective Andersen samples by 91 and 63%, respectively. However, in sample 4, the Andersen sample is higher by about 49%. The 2-propanol fraction is present in the highest weight percent, from 4.8-6.8% in the Andersen particulate matter, whereas in contrast in two samples, 2 and 3, the hexane-benzene fraction is present in the highest weight percent, 5.6 and 5.9%, in the Hi-Vol samples.

These results are similar to those of the % fractions in TOM where the Andersen 2-propanol fractions represent the largest part, 70-73%, of the TOM, whereas the Hi-Vol hexane fraction represents 20-52% of the TOM. In the breathable particulate matter, no methanol or cold and hot acetone fractions were found. This is not surprising considering the low level of these fractions in Hi-Vol samples and the small masses of the Andersen particulate samples (Table III, footnote c). The fractions containing oxygenated species—i.e., chloroform, 2-propanol, methanol, and cold and hot acetone (Table II) are combined and designated the oxygenated fraction (Table IV). There are some differences between percent weight distribution of this oxygenated fraction in the parallel collection experiments—i.e., in Experiments 3 and 4, the Andersen oxygenated fractions are larger by 6.4 and 71%, respectively, whereas in Experiment 2 the Hi-Vol oxygenated fraction is greater by about 25% (Table IV). These mixed results do not show any clear cut trend.

Another way of evaluating the oxygenated fractions is by comparing their percent weight distributions in the TOM. For samples 2, 3, and 4, the oxygenated substances amount of 88.8, 83.5, and 92%, respectively, for the Andersen particulate samples, while those for the corresponding Hi-Vol samples are 58, 48, and 80%, respectively (Table IV). Wynder and Hoffmann (4) found about 40% oxygenated materials in Hi-Vol samples, whereas Tabor et al. (26) indicate a range of 12-38% of oxygenated substances in benzene-extracted total organic matter, collect-

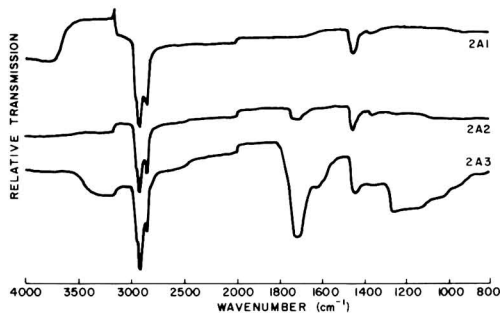


Figure 2. Infrared curves of organic fractions in Andersen sample from Experiment 2. Fraction designations are: 2A1, hexane-benzene; 2A2, chloroform; and 2A3, 2-propanol

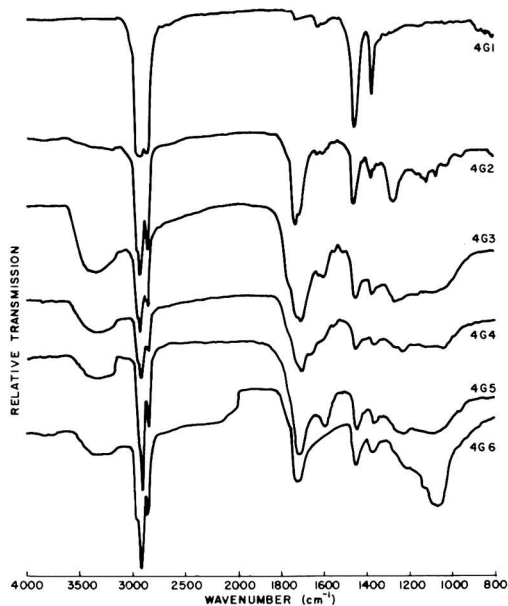


Figure 3. Infrared curves of organic fractions in Hi-Vol (Gelman) samples from Experiment 4. Fraction designations are: 4G1, hexane-benzene; 4G2, chloroform; 4G3, 2-propanol; 4G4, methanol; 4G5, acetone; and 4G6, hot acetone

Table IV. Percent Weight Distribution of Organic Fractions in Particulate Matter^a

Fraction, f	Experiments					
	2 (11/16-19/'71)		3 (12/20-22/'71)		4 (2/21-25/'72)	
	Hi-Vol (total)	Andersen (breathable)	Hi-Vol (total)	Andersen (breathable)	Hi-Vol (total)	Andersen (breathable)
Hexane-benzene	5.59	0.77	5.90	1.15	1.30	0.79
Chloroform	3.20	1.13	2.50	1.00	1.91	2.12
2-Propanol	3.69	5.06	2.60	4.83	2.20	6.79
Methanol	0.57	...	0.16	...	0.50	...
Acetone	0.21	...	0.22	...	0.20	...
Hot acetone	0.05	0.40	...
Total organic matter	13.31	6.96	11.38	6.98	6.51	9.70
Oxygenated ^b	7.72	6.19	5.48	5.83	5.21	8.91

^a % Fraction = $[\mu\text{g}/\text{m}^3 \text{ (fraction)}] / [\mu\text{g}/\text{m}^3 \text{ (particulate matter)}] \times 100$ (Table III). ^b This fraction is a combination of all except the hexane-benzene fraction.

ed from three cities, based on the amount of neutral, oxygenated, and weak and strong acid fractions recovered. Our analyses show the consistently high proportion of oxygenated organic substances in the total organic matter of the Andersen samples compared to Hi-Vol samples. This is an important consideration relative to the cocarcinogenic activity of oxygenated substances (4).

Two bases, particulate and total organic matter, are used to determine the % N, O, and carbonyl and double bond distributions. The computation for % N, O, and carbonyl and double bond distribution in particulate matter, PM, for fraction *f*, % (X_{PM})_{*f*} is as follows:

$$\% (X_{PM})_f = \frac{\% X(\text{emp})_f \times \% (\text{wt dist.})_f}{100} \quad (1)$$

Where % *X*(emp)_{*f*} refers to the % O and N determined from the empirical formulas of fraction, *f* (Table II), or to the ir ratio or number of double bonds (Table II) and % (wt distribution)_{*f*} for fraction, *f*, given in Table IV.

The % N, O, and carbonyl and double bond distribution in total organic matter (TOM), % (X_{TOM})_{*f*}, is calculated as follows:

$$\% (X_{TOM})_f = \frac{\% X(\text{emp})_f \times AC_f}{AC(\text{TOM}) \times 100} \quad (2)$$

Where AC_{*f*} is the atmospheric concentration of fraction, *f* (Table III), and AC(TOM), the atmospheric concentration of the TOM for the particular experiment (Table III).

Oxygen contained in hydroxyl and carbonyl groups is present in all but the hexane-benzene fraction as indicated by ir and uv spectroscopy (1) (Figures 2 and 3). The % O in particulate matter for various fractions is listed in Table V. The total % O is quite similar in the parallel experiments varying from 1.06-1.33%. In experiments 2 and 4, the % O for the Andersen samples are 8 and 10% larger, respectively, than the Hi-Vol particulate matter. However, a comparison of the distribution of oxygen in the two fractions, chloroform and 2-propanol, shows some definite trends. The chloroform fractions show a paucity of oxygen for the Andersen samples. The Andersen 2-propanol fractions in two experiments, 2 and 4, are 90 and 98% higher, respectively, than their corresponding Hi-Vol fractions. In Experiment 3, the Hi-Vol fraction is higher by 20%. There seems to be a trend of low oxygen content in Andersen chloroform fractions and high oxygen content in Andersen 2-propanol fractions. The % O in TOM (Equation 2) shows results similar to those for the particulate matter. Notably the Andersen 2-propanol fractions are higher than their Hi-Vol counterparts by about 34-260%.

The % N distribution based on both particulate matter (Table VI) and total organic matter show the same general trends. In all experiments the hexane-benzene and 2-propanol Andersen fractions have higher % N values than the Hi-Vol samples by substantial amounts. The total % N values for each experiment show the much higher content of nitrogen in particulate and total organic matter for Andersen samples relative to Hi-Vol samples. These increases range from 65-680% and show the higher level of nitrogenous substances present in separate fractions and the total samples from the Andersen experiments.

In the calculation of the % distribution of the carbonyl functional group, the ir absorbance ratio [$C=O/C-H$ (1)] is used to represent the percent carbonyl in the various fractions. In experiments 2 and 3 the total percent carbonyl in particulate matter is greater in Hi-Vol samples by about 60 and 19%, respectively (Table VII). However, the opposite is true in Experiment 4, the Andersen value being larger by 76%. The 2-propanol fraction contains substantially higher percent levels of carbonyl in

Table V. Percent Oxygen Distribution in Particulate Matter^a

Expt	Fractions			Total
	CHCl ₃	2-Propanol	Other fractions	
2G	0.36	0.61	0.12 ^b	0.09
2A	0.00	1.17	... ^c	1.17
3G	0.38	0.59	0.09 ^b	1.06
3A	... ^d	0.49	... ^c	...
4G	0.28	0.61	0.27 ^b	1.16
4A	0.12	1.21	... ^c	1.33

^a See Equation 1. The benzene fraction contains no oxygen. ^b Percent oxygen distribution for methanol and acetone fractions for 2G are 0.08 and 0.04%, and for 3G are 0.06 and 0.03%, respectively, while the methanol, acetone, and hot acetone fractions for 4G are 0.15, 0.02, and 0.10%, respectively. ^c No fraction detected. ^d Insufficient sample for analysis.

Table VI. Percent Nitrogen Distribution in Particulate Matter^a

Expt	Fractions				Total
	Hexane-benzene	CHCl ₃	2-Propanol	Other fractions	
2G	0.04	0.05	0.08	0.05 ^b	0.22
2A	0.13	0.02	0.23	... ^c	0.38
3G	0.06	0.02	0.06	0.02 ^b	0.16
3A	0.16	... ^d	0.21	... ^c	0.37 ^e
4G	0.02	0.03	0.06	0.09 ^b	0.20
4A	0.20	0.42	0.94	... ^c	1.56

^a See Equation 1. ^b % N distributions for methanol and acetone fractions for 2G are 0.04 and 0.01%, and for 3G are 0.008 and 0.02%, respectively, while the methanol, acetone and hot acetone fractions for 4G are 0.02, 0.02 and 0.05%, respectively. ^c No fraction detected. ^d Insufficient sample. ^e CHCl₃ value missing.

Experiments 3 and 4 for the Andersen samples. In all experiments, the total percent carbonyl in the total organic matter is higher in the Andersen samples by 20-34%, while the 2-propanol fractions of the Andersen samples are higher than their Gelman counterparts by 63-105%. In general, the Hi-Vol chloroform fractions show higher levels of carbonyl in the particulate and total organic matter than their parallel Andersen fractions by substantial percentages.

The semiquantitative estimation of the number of double bonds for a fraction utilizes the corresponding empirical formula and allows for a correction assuming that all oxygen is present as the carbonyl group (Table II, note b). Since hydroxyl groups are also present, the assumption can lead to an overcorrection or a smaller number of double bonds (Table II, note e). (Hydroxyl groups lead to no oxygen correction.) The presence of both secondary and tertiary (polynuclear azaheterocyclic substances) nitrogen-containing organic compounds (16, 27, 28) suggests a correction for nitrogen. However, since each of these forms calls for a correction in the opposite sense and no information is available on their relative distribution in particulate matter, no nitrogen correction was made. Table II shows that the Andersen samples have a much higher degree of unsaturation than the corresponding Hi-Vol samples. The acetone fractions also possess a high degree of unsaturation. A calculation of double bond content distribution in particulate matter using the number of double bonds for % *X*(emp)_{*f*} in Equation 1, shows the Andersen 2-propanol fractions with an overwhelmingly high level of double bond content compared to all other fractions for both collection techniques. Also each of the total Andersen samples contains a larger content of double bonds than the Hi-Vol samples. This same result is more accentuated when double distribution in TOM is computed using Equation 2.

In Figures 2 and 3, typical ir curves for Andersen (Experiment 2) and Hi-Vol (Experiment 4) samples are illustrated. Because the curves represent mixed spectra, individual compounds can't be identified, only functional groupings. Due to the superposition of some functional group vibrations, care must be taken in interpretation of mixed spectra. However, from the empirical formulas and the ir curves some conclusions can be drawn.

The strong C—H absorptions are below 3000 cm^{-1} indicating the presence mainly of aliphatic hydrocarbons. However, there are weaker absorptions between 3000 and 3100 cm^{-1} indicating the possible presence of polyaromatic (polynuclear) hydrocarbons. The fractions showing these absorptions are 4G1, 2, 3, and 5; 4A2; 3G1, 2 and 5; 3A2; 2G1 through 6; 2A1 and 1A1 through 3.

Hydroxyl absorptions are not observed in hexane fractions and in very low concentrations in chloroform fractions of Andersen samples, 1A2 through 4A2 (Figure 2 for 2A2). All other fractions contain discernible levels of hydroxyl absorption at about 3200–3300 cm^{-1} and also carbonyl absorption (presence of a shoulder) at about 1750–1760 cm^{-1} (Figures 2 and 3). All fractions other than the hexane fractions have carbonyl absorptions in the range 1735–1700 cm^{-1} . Carboxylic acids in their dimeric form have carbonyl absorptions in the range 1725–1700 cm^{-1} and hydrogen-bonded hydroxyl absorptions in the range 3300–2500 cm^{-1} , while the monomeric acids have hydroxyl and carbonyl absorptions at about 3500 cm^{-1} and 1760 cm^{-1} , respectively. Also saturated aliphatic ketonic and aldehydic carbonyl absorptions are in the ranges 1725–1705 cm^{-1} and 1740–1720 cm^{-1} , respectively (29).

With the above norms the content of the various fractions can be summarized. Fractions 1, 2, and 3A2 contain mainly aldehydes and ketones; 4A2 contains mainly aldehydes; 2G3, 3G3, 3G5, and 4G4 contain acids and ketones; and 1A3 through 4A3, 2G2, 2G4 through 2G6, 3G2, 3G4, 4G2, 4G3, 4G5, and 4G6 contain acids, aldehydes, and ketones. This is not surprising since the polymerized oxidized hydrocarbons present in these samples would contain a variety of hydroxy and acidic groupings (1).

It should be noted that the carbonyl absorptions are quite broad in some instances (fractions 4G3 and 4G4 in Figure 3). Another group of absorptions are present at 1655, 1620, 1600, and 1595 cm^{-1} . These vibrations indicate along with the empirical formula the possible presence of oximes, 1660–1630 cm^{-1} , other organic nitrogen substances, and conjugated diketones or unsaturated carbonyl compounds (29). There is evidence in some of the ir spectra of ring-stretching vibrations for heterocyclic rings such as in polynuclear aza heterocyclic compounds (29).

These data suggest the presence of a number of substances found in benzene extracts of particulate matter. Several polynuclear aza heterocyclic substances, such as

benzoquinolines and substituted derivatives, benzacridines and substituted derivatives, and dibenzacridines and substituted derivatives, were found. Dibenz(*a,h*)acridine and dibenz(*a,i*)acridine are carcinogenic while the carcinogenicity of some of the other aza compounds have not been finally established (16, 27). However, automobile exhausts contribute to a small percentage of the polynuclear aza heterocyclic substances in air (30). Sawicki (27) has reported the presence of polynuclear carbonyl substance such as anthanthrone, xanthen-9-one, 9-acridanone 7H-benz(*de*)anthracen-7-one, and others. There is some disagreement about the carcinogenicity of the latter (27, 28).

Conclusion

Cukor et al. (1) reported that organic matter, extracted and separated by the techniques herein described, contained mainly oxidized, polymerized hydrocarbons and some nitrogenous compounds with an average molecular weight of 330 and empirical formulas similar to those given in Table II. An empirical formula reported by Sawicki et al. (31) for a composite benzene-extracted fraction taken from samples representing 200 American communities is as follows:



In this formula OR represents alkoxy, while X is the halogen content expressed as chloride. This formula and the calculated double bond content of 8 (Table II, note *b*) correspond closely to some of the data given in Table II. An average molecular weight of 468 was obtained by Sawicki et al. (31), which is somewhat larger than that reported by Cukor (1).

The formation of oxidized, polymerized hydrocarbons and nitrogenous azaheterocyclic substances in particulate matter may be explained as follows: The presence of reactive organic substances in exhaust gases (32–40) and nitrogenous materials as alkyl amines (41), methyl nitrate and some nitrites (37), coupled with the pyrosynthetic action in the automobile engine (32, 34, 35), leads to the variety of the polymerized, oxidized hydrocarbons (1) and nitrogenous materials (Table II) found in particulate samples. Also, the role of lubricating oil and gasoline and lubricating oil additives should not be overlooked. A wide variety of compounds are used as additives and their role in pyrosynthetic reactions and particulate formation is an important consideration (42). Dubois et al. (43) have shown that oxidized lubricating oil may be exhausted as aerosols [see also Cukor et al. (1)].

The particulate matter collected in the Andersen sampler, stages 2–7 (breathable particulate matter), represents 55, 50, and 28% of the particulate matter deposited in the NP, TB, and P lung compartments, respectively. The organic compounds extracted from the particulate matter from stages 2–7 show a much different composition from that of the total particulate matter collected by the Hi-Vol sampler. In particular, the 2-propanol chromatographic fraction containing oxygenated and nitrogenous substances represented a higher concentration level in the breathable particulate matter. As indicated by a number of investigators (12–15), the concentration of inorganic constituents is a function of particle size of particulate matter. The results obtained in the organic analysis of breathable and total particulate matter seem to indicate a similar relationship for organic substances as for inorganic compounds. This finding bears directly on the types of substances found in the lung compartments and, through the clearance mechanisms (17), indicates the possible paths of contamination in the body.

The 2-propanol fraction contains the most polar organic

Table VII. Percent Carbonyl Distribution in Particulate Matter^a Fractions

Expt	Fractions			Total
	CHCl ₃	2-Propanol	Other fractions	
2G	1.31	3.88	0.97 ^b	6.16
2A	0.11	3.75	...	3.86
3G	1.25	2.34	0.34 ^b	3.93
3A	0.27	3.04	...	3.31
4G	0.71	1.98	0.74 ^b	3.43
4A	1.29	4.75	...	6.04

^a See Equation 1. ^b Percent carbonyl distributions for methanol, acetone, and hot acetone for 2G are 0.78, 0.15, and 0.04% and for 4G are 0.48, 0.10, and 0.16%, respectively, while the methanol and acetone fractions for 3G are 0.16 and 0.22%, respectively. ^c No fraction detected.

substances in the breathable particulate matter. These substances would most easily be extracted from deposited particulate matter by the aqueous secretions of the body. The composition of the 2-propanol fractions from the Andersen experiments indicates high levels of nitrogenous substances, possibly aza heterocyclics (16, 27), carbonyl groups [present in acids, aldehydes, and ketones, and possibly polynuclear carbonyl compounds (27)] and unsaturation relative to the corresponding Hi-Vol 2-propanol fractions and other Andersen and Hi-Vol fractions. Recently Zikria (44) suggested that aldehydes are the causative agent in smoke poisoning from results obtained in experiments on dogs. He postulated that it was reasonable to impute a cumulative effect during long-term exposure due to the denaturation of RNA and amino acids by aldehydes. Opie (45) has shown a relationship between a compound's ability to denature a protein and its effectiveness in causing necrosis and inflammation in living tissue. In addition, acids and oxygenated neutral organic fractions have been shown to have tumor-promoting activity on initiated skin (4,46). Thus, the strong indication is that the oxygenated fractions, present in highest concentrations in breathable particulate matter, and particularly the 2-propanol fraction, contain substances deleterious to the health of man. The human insult of particulate matter should be judged, therefore, on the distribution of particle size and the concentration of oxygenated substances, which contain acidic and aldehydic functional groups, and nitrogenous substances which may include polynuclear aza heterocyclic compounds.

Acknowledgment

We gratefully acknowledge the oxygen analyses by Carmine Persiani and the aid of Charles D'Angelo in the elemental determinations.

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Received for review April 12, 1973. Accepted June 24, 1974.

Adsorption of Mercury from Aqueous Solutions by Polyethylenimine-Modified Wool Fibers

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■ When used in a packed column or a standing bath, polyethylenimine-modified wool (PEI-wool) had a substantially greater ability to adsorb mercury (Hg^2) from aqueous solution than unmodified keratin. A capacity of 3.3 meq/g was achieved within 30 min using solutions of 1000 ppm (Hg^2). Sorption from liquors passing through a column was rapid and effective at the 1-ppm level. The sorbed mercury was readily desorbed and the PEI-wool used repeatedly.

There have been several recent reports of the ability of protein fibers to adsorb mercury from aqueous solution (1-4), and the possibility of using them in effluent purification processes or for clinical purposes (5) has been discussed. Likewise, amine-modified cotton could adsorb mercury from solutions (6, 7). Here we report that the adsorptive capacity of wool for mercury (Hg^2) is substantially increased by polymerization of ethylenimine onto the fibers.

Experimental

PEI-Wool. Commercially scoured 64's quality Australian merino wool fibers (40 grams) were immersed (2 hr) in a 0.2% solution of ferrous ammonium sulfate (800 ml) and then squeezed before allowing to dry (48 hr) at 20°C. To the wool was added 0.25% hydrogen peroxide solution (600 ml) and ethylenimine (30 ml) (8). [Because of potential hazards from exposure to ethylenimine, it has been recommended (9) that protective gloves and goggles be used and that all operations be performed in a fume hood.] The fibers were heated (19 hr) at 50°C under nitrogen, rinsed under running tap water (2 hr), dried as before, and chopped to 1-3 mm lengths in a rotary mill. The uptake of ethylenimine (as bound PEI) was 10% w/w.

PEI-Reduced Wool. Unmodified wool (10 grams) was chemically reduced with 0.5M thioglycolic acid (300 ml) at 50°C for 3 hr, washed with distilled water, dried (100°C, 5 min), and converted to PEI-reduced wool as above. The uptake of ethylenimine (as bound PEI) was 20.2% (w/w).

Adsorption onto Columns of Chopped Wool Fibers. The wool (5 grams) was wet out in water containing 0.01% Antaron C0630 (a polyoxyethylated nonylphenol, GAF Corp.) and the resulting slurry poured into a glass column fitted with a porous plug and stopcock. When the fibers had settled they were equilibrated with solutions at the pH of the test solutions. The test solutions contained 1000 ppm Hg^2 (as HgCl_2 or a combination of HgCl_2 -NaCl, Table I) and adjusted to various pH values with NaOH or HCl. Test solutions were admitted at the rate of one bed volume/min. The column effluent was collected in fractions and their mercury concentration measured.

Adsorption onto Wool in Standing Bath. The wool (5 grams) was stirred in a glass beaker with a solution (1 liter) adjusted to the required pH, containing 1000 ppm Hg^2 (as HgCl_2 or HgCl_2 -NaCl, Table I) for prescribed periods.

Capacity of Wool Fiber Beds. Here the capacity of the beds has been expressed as milliequivalents of mercury per gram of wool (meq/g). For adsorption onto columns it

was the amount of mercury adsorbed by the bed when its concentration in the column effluent reached 1% of the influent concentration. For adsorption onto wool in standing baths it was the amount adsorbed from the liquors after the prescribed period, and the value was calculated from the decrease in mercury concentration of the bath liquor. All adsorption measurements were made at 20°C.

Mercury Analysis. This was by atomic absorption spectrophotometry. Separate procedures used for solutions containing 1-1000 ppm (10) and up to 1 ppm Hg^2 (11) were essentially as described.

Results and Discussion

PEI-Wool. Protein fibers will bind approximately 1% of polyethylenimine irreversibly (12). This quantity will increase slightly if the fibers are pretreated with chlorine. By polymerization of ethylenimine monomer onto wool fibers, as reported here, irreversible binding of 10-20% PEI can be achieved. It is not known whether the PEI-wool composite so formed contains the PEI as a physically occluded or chemically grafted component. In the present work, wool treated by the last method has been used as packed beds in columns and in stirred standing baths to examine its potential in both continuous and batchwise mercury recovery processes.

Table I shows that maximum adsorption occurred in standing baths where, within 30 min, equilibrium was established. The capacity of 3.3 meq/g is of the same order as that of many granular ion exchangers. Even in solutions containing 10% NaCl, the adsorption of 1 meq Hg^2 /g was still significant and may indicate that PEI-wool could

Table I. Mercury Adsorption by Polyethylenimine-Modified Wool

Liquor pH	Experimental methods ^a	NaCl concn., %	Capacity, meq Hg^2 /g wool
PEI-Wool			
6	S_{30}		3.3
6	S_{60}		3.3
6	S_{15}	10	1.0
6	S_{60}	10	1.1
6	S_{15}	25	0.6
6	S_{60}	25	0.6
2	C		1.4
7	C		2.4
6	C	25	0.2
PEI-Reduced Wool			
6	S_{30}		3.6
6	S_{60}		3.6
6	S_{45}	3	2.0
6	S_{30}	10	1.1
6	S_{30}	25	0.9
7	C		2.8
6	C	3	1.6
Unmodified Wool ^b			
6	S_{60}	25	0
2	C		0.58
7	C		0.29

^a S with a numerical subscript refers to adsorption in a standing bath for the indicated period (min); C refers to a column adsorption.
^b From (7).

have practical advantages in adsorbing mercury from electrolyte solutions (13).

In column adsorption tests, where the contact time was 1 min, the capacity was lowered slightly to 2.4 meq Hg²⁺/g at pH 7, indicating that adsorption was a rapid process. Sorbed mercury was quantitatively recovered by extracting the PEI-wool with N HCl (50°C, 15 min) or with citric acid solution (1%, pH2, 40°C, 15 min). The wool that was stripped in this way could be reused, an adsorption capacity of 2 meq/g persisting after 15 cycles.

Adsorption onto columns was effective when low concentrations of mercury were used. When 500-bed volumes of liquor containing 1 ppm Hg²⁺ (pH 6) were passed through the column (1 bed vol/min), the concentration in the effluent did not exceed 0.02 ppm. Greater efficiency could be expected from longer contact times in the column.

When we consider the pH range 2-7, we note that modification of wool with PEI changes the pH of maximum adsorption from 2 to 7; corresponding differences in the adsorption mechanisms might be inferred. Probably, at pH 2, the association of protonated amino groups with anionic mercuric complexes such as HgCl₃⁻ or HgCl₄²⁻ occurs (1). At pH 7, the adsorption probably involves chelation of Hg²⁺ with ligands located in both the PEI (14) and the wool.

PEI-wool appears to have a mercury adsorbing capacity exceeding cross-linked PEI-cotton (6) by a factor of 100. Although strict comparisons have not been made its rate of adsorbing mercury seems substantially greater than that reported for the modified cotton (7).

PEI-Reduced Wool. Ethylenimine was polymerized onto thioglycollate-reduced wool in the expectation that the chemically modified fibers, released from the restraint

of protein disulfide bonds, would swell more readily in aqueous media. An increased PEI add-on and correspondingly improved mercury adsorption might then have resulted.

Practically, the amount of PEI formed in reduced wool was double that formed in native wool. Only minor increases were observed in the mercury-adsorbing capacity of PEI-reduced wool, consequently no advantage can be seen in using wool in the reduced form.

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Received for review November 6, 1973. Accepted May 3, 1974.

Removal of Mercury from Aqueous Solutions by N-(2-Aminoethyl)aminodeoxy cellulose Cotton

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■ N-(2-Aminoethyl)aminodeoxy cellulose cotton (AEAC) was prepared in yarn form by reaction of ethylenediamine with chlorodeoxy cellulose. The adsorption of mercuric ion by AEAC (degree of substitution 0.4) was studied over a wide range of concentrations. In the concentration range 0.5-43 g/l., the adsorption of mercuric chloride follows the Freundlich relationship, $\log_{10} x = 0.21 \log_{10} C + 2.7$, where x is the mg of mercuric chloride bound per gram of AEAC and C is the residual concentration in g/l. At concentrations in the range of 3.1-0.6 ppm, 100 mg of AEAC removed about 90% of the mercury present in 200 ml of solution, in a single equilibration. The results of this study suggest the possible use of AEAC as an agent for the collection of mercury in industrial processes.

The possibility of employing ion exchange or chelating resins as a means of removing heavy metal ions from solution has been explored by a number of workers (1-5). However, cost considerations have prohibited the widespread application of this technique on an industrial scale. A possible solution to the cost problem might be to use naturally occurring polymers or agricultural by-pro-

ducts as the basis for the exchange resin. In this regard, Friedman and coworkers (6, 7) have shown that mercuric ion is bound in large amounts by certain agricultural by-products and polyamine derivatives.

This investigation concerns the use of cotton cellulose as the insoluble support matrix; however, the same techniques could be readily applied to other celluloses or synthetic polyalcohols. In the study reported here, we have attached an ethylenediamine group to the anhydroglucose unit of the cellulose backbone via chlorodeoxy cellulose (CDC) cotton yarn to give N-(2-aminoethyl)aminodeoxy cellulose cotton (AEAC). AEAC very efficiently adsorbs mercury over a broad range of concentrations. Surprisingly, we observed that at very low concentrations (approximately 100 ppb), untreated cotton yarn also removes significant amounts of mercury. This adsorption may be due to carboxyl end groups and trace materials present in native cotton.

Experimental

Materials. Cotton was loose twist 12/3 (tex-151) Pima kier-boiled yarn unless otherwise specified. The phosphorus oxychloride (POCl₃), dimethylformamide (DMF), and

ethylenediamine were commercial reagent grade chemicals used without further purification. The water was purified by mixed bed-ion exchange chromatography.

Synthesis of Cotton Derivatives

Chlorodeoxycellulose. This material was prepared by the method of Vigo and Welch (8). The cotton yarn (15.02 grams) was activated for chlorination by preswelling in DMF for 30 min. Chlorination was achieved by immersing the yarn in 24% POCl₃-DMF (w/w) at 75° for 15 min; the bath ratio was 40 grams solution per gram of cotton. The reaction vessel was then cooled in an ice-water bath to room temperature and successively washed for a period of 15 min with each of the following: DMF; tap water; 5% sodium hydroxide; tap water; 5% acetic acid; and, finally, tap water. After equilibration at ambient conditions for 48 hr, the yarn was weighed (16.9 grams or 13.1% weight increase). This sample gave the following analysis (wt %): Cl, 10.43; N, 0.31; P, 0.85.

This percent chlorine corresponds to a degree of substitution (DS) of 0.50 chlorine atom per anhydroglucose unit.

N-(2-Aminoethylaminodeoxycellulose) (AEAC). A slight modification of the procedure of Vigo et al. (9) was used in the synthesis of this material. Conversion of the chlorodeoxycellulose described above was accomplished by immersing the skein (16.08 grams) in neat ethylenediamine (350 ml) at 100°C for 3 hr. At the end of this time, the reaction vessel was immersed in an ice-water bath and cooled to room temperature. The sample was removed and washed for a 15-min period with ethanol followed by a tap water rinse. After oven drying at 80°C for 15 min and equilibration at ambient conditions for 24 hr, the weight was 17.02 grams. Analysis: Cl, 1.59; N, 6.45; P, 0.65 (wt %).

From the percent nitrogen, the number of ethylenediamine groups included per anhydroglucose unit (DS) was calculated as 0.40.

Adsorption Experiments

Whenever AEAC yarn was employed, the DS was 0.40. The amount of mercuric chloride adsorbed from aqueous solution at "high" concentration (0.075–5.0% HgCl₂) was calculated by the weight gain of the yarn at the completion of a run. In a typical experiment, a piece of yarn weighing approximately 500–600 mg was immersed in a known volume (100–1000 ml) of aqueous mercuric chloride of known concentration and shaken for 24 hr.

At the end of this time, the sample was removed from the solution, washed with deionized water for a period of 3–4 sec, and weighed after drying at ambient conditions for 24 hr.

When experiments were conducted at low concentration (118–3100 ppb Hg²⁺), equilibration was accomplished by immersing a 100-mg sample in 200 ml of aqueous mercuric chloride of known concentration for 24 hr. After the adsorbent was removed (by filtration when ground material was used), the solution was assayed for mercury by flameless atomic absorption with a Coleman Model MAS-50 analyzer. All samples were analyzed within 24 hr after the completion of a run.

Results and Discussion

The investigation showed that CDC yarn, which can now be obtained in high DS by a rapid and convenient synthetic technique (8), was converted in good yield (80–85%) to the corresponding AEAC by reaction with neat ethylenediamine. Our initial goal was to attach a bidentate ligand (such as ethylenediamine) in such a manner as

Table I. Adsorption of Mercuric Chloride by N-(2-Aminoethyl)aminodeoxycellulose Cotton Yarn (AEAC) at High Concentration^a

Sample	Initial, ppb	Final, ppb
Cotton	3100	2700
AEAC	3100	240
Cotton	616	198
AEAC	616	62
AEAC ^b	616	37
Carboxymethylcellulose cotton ^c	616	340
Dialdehydecellulose cotton ^c	616	500
AEAC ^d	616	100
Cotton	118	38
Cotton ^e	118	39
AEAC	118	48
AEAC ^b	118	31
AEAC ^d	118	40

^a Sample is in yarn form and the AEAC/volume ratio is 100 mg/200 ml unless otherwise specified. The DS is 0.40. ^b Ground in a Wiley Mill, 20 mesh. ^c Printcloth. ^d 125-mg yarn in 500-ml solution.

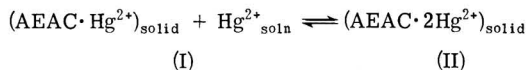
to maximize the DS, while minimizing the amount of cross-linking. In doing so, it was felt that the physical constraints of the polymer backbone on the ligand would also be minimized, thus allowing the ligand a greater degree of freedom in assuming the most favorable coordination geometry. From the elemental analyses, it was estimated that approximately 25% of the ethylenediamine groups are cross-linked to cellulose.

Results showing the amount of mercuric chloride adsorbed as a function of initial solution concentration in the range 0.075–5.0% mercuric chloride are collected in Table I. From these results, it is readily seen that the AEAC is capable of adsorbing approximately its own weight in mercury. When these data are treated by a linear regression analysis according to the Freundlich adsorption isotherm, the following relationship is obtained.

$$\log_{10} x = 0.21 \log_{10} C + 2.7 \quad (1)$$

where x is the amount of mercuric chloride adsorbed by the AEAC (DS 0.40) in mg/g yarn and C is the equilibrium concentration of mercuric chloride in g/l. The correlation coefficient was calculated as 0.991.

Examination of Table I further reveals that, in the concentration range studied, the g-atom mercuric chloride bound per g-atom N present in the AEAC varies from 0.46–1.14. This would indicate that Equation 1 is describing the following process involving the binding of the second mole of mercuric ion:



The ratio of g-atom of HgCl₂/N would of course be expected to vary between 0.5 and 1.0 if one were observing the transformation of (I) to (II). The high value of 1.14 given in Table I is probably reflecting the presence of water of hydration.

Table II shows the ability of AEAC to remove mercury at low initial concentrations (3.1 ppm–118 ppb). The table shows that 100 mg of AEAC yarn in 200 ml of 3.1 ppm mercuric ion reduces the mercury concentration to 240 ppb (13 fold or 92%) in a single equilibration. Holding the AEAC/volume ratio constant but lowering the concentration fivefold to 616 ppb reduces the efficiency only slightly—to 90%. However, when the concentration is again lowered by a factor of 5, to 118 ppb, the efficiency decreases to only 59%. More surprising was the finding

Table II. Mercury Adsorption by N-(2-Aminoethyl)aminodeoxycellulose Cotton (AEAC) at Low Concentration^a

Vol. l.	Initial concn, HgCl ₂ in g/l.	Residual concn, HgCl ₂ in g/l.	Mg HgCl ₂ bound/g-AEAC	G-atom HgCl ₂ bound/g-atom N
1.0	0.75	0.49	574	0.46
1.0	1.00	0.73	607	0.48
1.0	2.00	1.66	646	0.52
1.0	3.00	2.63	730	0.58
0.2	5.00	3.04	823	0.66
0.5	8.00	6.90	949	0.76
0.1	20.0	15.1	1060	0.85
0.1	30.0	23.8	1220	0.98
0.1	40.0	33.1	1340	1.07
0.1	50.0	42.9	1430	1.14

^a The sample was 500-600 mg of AEAC yarn having a DS of 0.40.

that cotton was about equally effective in removing mercury at this exceedingly low concentration, though it is clear from the results collected in Table II that the number of tight binding sites present on native cotton are limited. The ability of unmodified cotton to bind certain metal ions has been observed by others (10). These workers showed that Ce⁴⁺ and Fe³⁺, in particular, were very strongly bound to cellulose. However, the exact nature of the binding was not elucidated. It appears that Hg²⁺ may be bound to native cellulose by the same mechanism as are the Ce⁴⁺ and Fe³⁺ ions. The binding may be due to carboxyl end groups present in the cellulose and to trace amounts of nitrogenous materials or other impurities in the cotton. Until the effect of impurities on the binding of metals at low ppb concentrations by cotton is studied, more definite conclusions cannot be drawn.

It has been pointed out by others that cotton derivatives might be amenable to a continuous belt process (1, 4). Although AEAC was investigated as a possible material for pollution control at low mercury levels (below 1 ppm), its capacity to bind large amounts of mercury make it potentially useful in a continuous extraction procedure where it is necessary to remove large quantities of heavy metal ions. Several elution procedures already reported in the literature, such as the use of EDTA or sodium thiocyanate (4) or the use of strong mineral acids (11) could be employed to remove the adsorbed mercury from the AEAC cotton.

Acknowledgment

The authors wish to express their gratitude to Mrs. Nancy Morris for making the atomic adsorption measurements.

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Received for review August 31, 1973. Accepted May 2, 1974. Mention of commercial products is for identification only and does not constitute endorsement by the U.S. Department of Agriculture.

INDUSTRY TRENDS

Ajax International Corp. will install a water purification and recycling plant, worth almost \$7 million, and including reverse osmosis treatment equipment, for Swissair. The facility will purify water from the airline's engineering facility, as required by law.

Predicasts, Inc., Cleveland, Ohio, predicts that in 1985, total value of shipments of plumbing fixtures and fittings could reach \$2.7 billion, an increase of 7.6% annually over 1972 levels.

Limnetics, Inc., a subsidiary of Carus Corp., received an environmental management contract for the Rio Blanco oil shale project, a joint venture of Gulf Oil Corp. and Standard Oil Co. (Ind.). The Rio Blanco group hopes to process shale oil by 1980.

United States Filter Corp. announced income for the second quarter of 1974 of \$2,194,000, or \$0.27/share, as compared with \$1,871,000 or \$0.23/share for the like period of 1973.

Standard Havens, Inc. has shipped seven reverse pulse baghouses which are to control emissions of fly ash at Du Pont's Parkersburg, W.Va., plant, an industrial boiler house with a 120-MW capacity equivalent.

Aerodyne Development Corp.'s Type "S" dust collectors are enabling Celotex Corp.'s hardboard products plant at Paris, Tenn., to meet Tennessee's air pollution control regulations. Two such collectors were installed.

Dames & Moore, Los Angeles, Calif., is completing an environmental study for a U.S. Army Corps of Engineers maintenance dredging program in the Yaquina River and Bay, the Siuslaw River estuary, and the Umpqua and Smith River estuaries, Oregon.

Fluor Engineers and Constructors, Inc. will be the engineering contractor for a coal gasification facility to be built in Dunn County, N.D., by Natural Gas Pipeline Co. of America, Chicago, Ill.

Osmonics, Inc. announced sales of \$415,334 for the six months ended June 30, 1974, as compared to \$331,984 for the like period of 1973. Net income before taxes was \$45,590 for the first six months of 1974, as compared to a \$33,694 loss for the first half of 1973.

Modern Talking Picture Service, Inc., New Hyde Park, N.Y., is offering free loan of "A Beginning," a 13½-min film, produced by the U.S. Office of Education, which shows people of different ages how they can help improve the environment.

Leeds & Northrup Co. will provide its LN5400 digital computer control system, utilizing two of the company's CP400 central processors and an analog system, to regulate the operation of the Upper Occoquan Sewer Authority's wastewater treatment plant at Manassas Park, Va.

Johns-Manville is making its new research and development center near Denver, Colo., and its equipment and experience, available to others on a contract basis. Expertise includes water and liquid waste treatment.

Dravo Corp. received a \$1.7 million contract to design and build an advanced wastewater treatment system for The Celotex Corp.'s gypsum and paperboard plant near Quincy, Ill. The system will meet Illinois' stringent requirements.

Combustion Engineering, Inc. (CEI) received an order of over \$20 million for a 350-MW steam generator and an air quality control system to remove SO₂ from flue gases. Southwestern Public Service Co., Amarillo, Tex., will receive this new equipment.

Ferro-Tech, Inc. made an agreement with Southern Engineering Services Pty. Ltd., Wollongong, Australia, to market Ferro-Tech's line of agglomeration systems and equipment in Australia and New Zealand.

The Automotive Testing and Analysis Div. of Hercules, Inc. is establishing a new district office in the Hercules Southfield, Mich., office complex.

Harza Engineering Co., Chicago, will study four alternative schemes for the rehabilitation of Lock and Dam No. 1, on the Mississippi River between Minneapolis and St. Paul, Minn., for the U.S. Army Corps of Engineers.

Clow Corp. is increasing sales of field-erected circular waste treatment plants capable of treating 100,000-1.5 million gpd of domestic sewage. Customers include small communities, mobile home developments, and residential subdivisions.

The Permutit Co. has installed a "PermuRO" reverse osmosis water treatment system to process brackish water at Arabian American Oil Co.'s crude oil refinery at Ra's at-Tanura, Saudi Arabia.

Goodyear is investing \$3.8 million in air pollution control devices to be installed at Goodyear's coal-burning power plant in Akron, Ohio. The equipment will remove about 73 million lb/yr of fly ash from the air.

EcolSciences, Inc., Vienna, Va., has received over \$200,000 worth of contracts from the EPA and the U.S. Soil Conservation Service for environmental studies in the District of Columbia, Maryland, Pennsylvania, and Virginia.

American Air Filter Co., Inc., was awarded a \$7.8 million air pollution control project contract by Republic Steel for their two 240-ton basic oxygen furnaces in Cleveland, Ohio.

Environmental Research & Technology, Inc., Lexington, Mass., will work on a large program for Dow Chemical Co. to conserve and preserve supplies of precious low-sulfur fuel.

Marco Pollution Control Corp., Seattle, Wash., was named U.S. representative for a line of Vikoma oil containment equipment made by Seaclean International (Surrey, England).

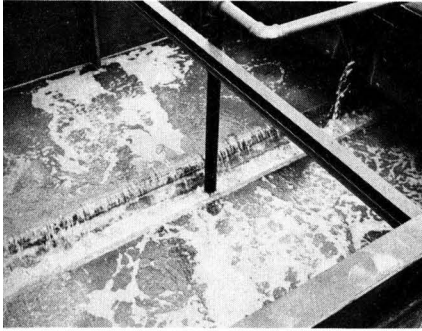
Research-Cottrell Inc. is building a fly ash scrubber system for backfit to an existing 55-MW pulverized coal boiler for Unit One of the Lewis & Clark Station of Montana-Dakota Utilities Co. near Sidney, Mont.

Skelly & Loy, engineers-consultants, Harrisburg, Pa., will carry out a nationwide study to develop coal mine effluent standards as required by the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500).

Ajax International Corp. has sold the largest reverse osmosis water treatment plant in Europe to supply over 1.3 million gpd of high-quality treated water to Cyanenka, S.A., a chemical complex near Barcelona, Spain.

SWECO, Inc. has announced the formation of the Screen and Filter Media Division. This new division will supply woven wire cloth and synthetic screens to customer specifications.

NEW PRODUCTS



Filtration systems

These systems are designed specifically for advanced and tertiary wastewater treatment. Prefabricated and on-site gravity and pressure types incorporate the latest technology in media beds, underdrain systems, and controls. Systems have numerous wastewater applications. Roberts Filter Mfg. Co. **101**

"The ecology bottle"

The bottle is made of glass recycled from old waste beer bottles and similar trash. Shaped like a stretch bottle, it can be used as a candle stick holder, vase, or simple decoration piece. Suggested retail price is \$0.99 each; a case of 24 weighs 18 lb. The Eclectic Co. **102**

Temperature indicator

Digital temperature indicator is low-cost, modular in construction, and contains socketed integrated circuits for ease of maintenance. Has easy-to-read 3-plus digit Sperry display. Useful in testing, research, and manufacturing. Calibration error is ± 2 digits plus conformity error. Leeds & Northrup **103**

Spectrophotometer/computer

New high-power device spectrographically and nondestructively locates wavelengths to define physical, chemical, and quality properties of almost all agricultural commodities. User is not burdened with the sophisticated optical technology, electronics, or computer and heavy mathematics involved. Data are available in seconds. Neotec **104**

Sterilizer

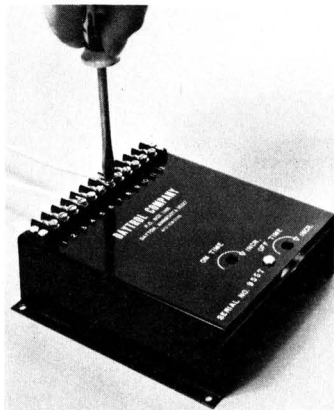
Low-cost bench-top sterilizer now automates sterilization and dispensing of agar in plates, tubes, or flasks. Sterilizes up to three liters of agar in 45 min or less with push-button ease. Useful in bacterial detection tests in hospitals and research and industrial quality control laboratories. New Brunswick Scientific Co., Inc. **105**

Oil spill detector

This system is practical for the detection and recovery of spilled oil. The device is floated in waters where spills may occur, and a water-excluding sensing membrane conveys oil to a calibrated sensor which actuates an alarm in a remote monitor. The alarm is sent by cable connection or VHF radio link. Durham Associates, Inc. **106**

Monitoring programmer

Programmer allows monitoring of up to 12 bins or containers with the use of a single central-level monitor electronics arrangement. It can sequentially interrogate sensor positions and determine material levels in each container. Useful in any process control system needing sequential operation of interrogation of several points. Wesmar **107**



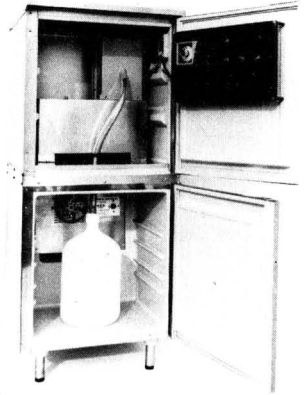
Program sequencer

Solid state program sequencer can be useful to dust collector users and manufacturers. It can replace conventional cam-type timers, offer up to 15 output terminals, and adapt to any function that will accept a momentary signal. Also useful to machine tool manufacture and use, and to other equipment requiring sequencing. Very compact. Daytrol Co. **108**

Gauge guard

Inexpensive brass-fitted pressure gauges can now be used on liquids highly corrosive to such metal. A diaphragm which separates the pressur-

ized liquid from the gauge eliminates the need for stainless steel or other more chemical-resistant materials. Gauge is installed in upper portion of cavity containing glycerin or other noncompressible fluid. Serfilco **109**

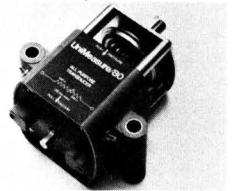


Wastewater sampler

Combination sampler and refrigerator collects wastewater samples and preserves their integrity in a refrigerated compartment. Handles flow capacities up to 50 gpm. Sample is provided with a 1-oz bucket-like scoop that can be programmed on a time or flow proportional basis. BIF SaniTrol **110**

Dust control system

Complete system picks up dust, chaff, and entrained dirt at all key dust-generating points of a grain mill. System includes hooding, ducting, cyclone precleaners, cloth separators, and exhausters, all sized and laid out for individual grain mill requirements. Dust nearly no more problem at truck unloading points and loadout pits. G. A. Kleissler Co. **111**



Pressure transducer

All solid state pressure transducer is designed for industrial testing and monitoring. Device offers infinite resolution and linearity and hysteresis errors of less than 1%. There are no parts subject to wear. No power supplies or amplifiers are needed. Output is read on any digital multimeter. UniMeasure **112**

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NEW LITERATURE

Oil skimmer. Full-color, six-page brochure details the MARCO Class I Oil Recovery System. Mechanical functions of the MARCO Fiberbelt principle and supporting equipment are explained and illustrated. MARCO Pollution Control 151

Environmental rooms. Bulletin No. 113E delineates a wide range of environmentally conditioned rooms that the company can provide. Temperature and humidity ranges are discussed; many applications are possible. Tenney Engineering, Inc. 152

Dust filter. Bulletins FT-503 and FT-503A describe and illustrate the operating principle and performance of a new dust filter which operates on a high-velocity, reverse-air cleaning system. Ferro-Tech, Inc. 153

NO-NO_x analyzer. Brochure describes the company's Model 14D dual chamber analyzer and Model 101 calibrator for ambient air concentrations of NO-NO_x. Principles of operation are described, and full specifications and capabilities are given. Thermo Electron Corp. 154

Pipe insulation. Bulletin describes "Thermazip," an insulation and protective jacketing that snaps onto pipes, ducts, tubes, and other lines simply and quickly. Accessible Products Co. 155

Water conservation. Six-page brochure is based on elimination of thermal pollution and conservation of water through use of efficient cooling water recovery systems. Ask for Bulletin S601/1-0. Baltimore Aircoil Co., Inc. 156

Heavy load moving. New brochure describes movement of massive loads of 1-2000 tons with the company's chain-action express rollers. Applications and operating techniques are given. Hilman Equipment Co., Inc. 157

Chlorine analyzers. Bulletin 1870 discusses the firm's "Series 870" chlorine residual analyzers for potable water and wastewater applications. A flow diagram is given, and typical applications are illustrated. Capital Controls Co. 158

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Leachate control. Twelve-page folder contains information on linings and covers, as well as general engineering suggestions. Lining materials are inert to leachates, and can be used under landfill material or as covers to prevent rainwater from percolating down. Request Bulletin 05144. Staff Industries, Inc. 160

Wastewater filtration. Bulletin 1000.1 discusses high-rate filtration practices in treating municipal wastewaters. Bulletin 1001.1 is specific as to the company's prefabricated wastewater gravity filter. Roberts Filter Mfg. Co. 161

Fuel oil treatment. Bulletin, "Gamlenol Dual Purpose for Diesel Engines," describes improved fuel oil atomization, sludging inhibition, corrosion inhibition, sulfur deposit suppression, and other benefits. Gemlen Chemical Co. 162

Exhaust fume control. Brochure, "Engelhard PTX Purifiers to Control Diesel Engine Exhaust Fumes," gives descriptions of different units, dimen-

sion and model data, operation details, and safety benefits. Engelhard Industries 163

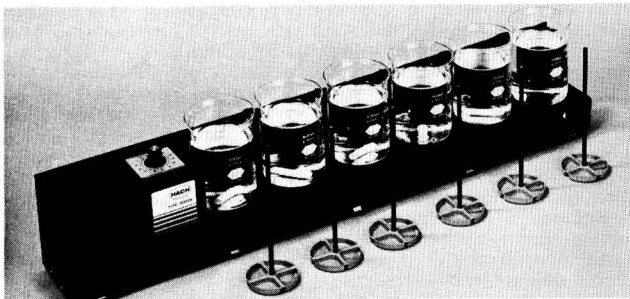
Water treatment. Form No. 1020 describes "Aquadene," a nontoxic, inorganic, crystalline compound for water treatment. Material will also slowly remove existing scale deposits. Stiles-Kem Corp. 164

NO stack monitor. Data sheet covers company's new Model 8A chemiluminescent analyzer for NO, for use where portability and sensitivity are important considerations. Thermo Electron Corp. 165

Baler. Four-page bulletin describes features and operation of the firm's "Cyclist 6-9" baler. Dimensions and specifications, as well as electrical requirements are set forth. Enviro Wasteaway, Inc. 166

Clarifier. Bulletin RC-74 features a multideck separator for continuous high-capacity dewatering of industrial and municipal wastes and processes. Kason Corp. 172

New jar test



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Water treatment. Booklet describing flocculants, settling operations, and clarification of water for municipal and industrial plants is available. Anionic, cationic, and nonionic flocculants are covered. Cyanamid International 182

Portable laboratory. Bulletin 8300 describes the company's portable water quality laboratory with which over 50 parameters can be tested. Equipment for doing colorimetric and titrimetric analysis is listed. Ecologic Instrument Corp. 183

Microcalorimetry. Bulletin describes the Series 300 QDTA modular system for quantitative differential thermal analysis and precise microcalorimetry. The device is sensitive to very minute energy changes. Features and applications are described. Fisher Scientific Co. 184

Particle counter. Bulletin about the company's Model 225/508 particle counter for ambient air analysis is now available. Royco Instruments, Inc. 185

Dump trailer. Data sheet describes the 23-TLH dump trailer which has many desirable adaptability features. Sargent Industries 186

Air pollution control. A 20-page, four-color brochure describes the company's expertise in this field, as well as packed towers, venturi scrubbers, adsorption, thermal oxidizers, and chemical reagents. Geo. A. Hormel & Co. 187

Viscosity control. Bulletin No. V-1290-A describes the company's line of viscosity control equipment. Norcross Corp. 188

Water chemistry. New facilities brochure describing applications for desalination plants, petrochemical and chemical process plants, refineries and utility plants, and steamships and motor vessels is available. Wet chemistry apparatus and company personnel and operations are covered. Bull & Roberts, Inc. 189

Water analysis. Pamphlet describes services available to industries and municipalities for analyzing water quality. Company's services in aiding in compliance with federal and state water analysis regulations are also described. J. P. Stevens & Co., Inc. 190

Particulate monitoring. Six-page brochure on the company's PM/ARGOS I particulate concentration monitor describes many performance-oriented features on a "beta-gauge" instrument system to monitor particulates from industrial sources. Lear Siegler 192

Sludge conditioning. Brochure on conditioning sludge from sewage, petrochemical wastes, paper and pulp wastes; and chemical wastes is now available. It tells how conditioning is done without the need for an open pit. Franklin Miller, Inc. 191

Diesel engine. New publication gives a complete description of the Model 25000 MARK II, 450-hp diesel engine, power unit, and electric set drive engine. An extremely low specific fuel performance map. Allis-Chalmers Corp. 193

Field testing. Company's services for environmental field testing and analysis, covering various aspects of air, water, and noise pollution sampling, are described in a new brochure. Particle Data Laboratories, Ltd. 194

Dewatering pumps. Four-color, 20-page catalog describes electric submersible dewatering pumps for the construction and mining industries. One type is explosionproof. Company facilities are described. Flygt Corp. 195

Current meters. Brochure describes the company's Model 700 electromagnetic water current meters, working on a two-axis electromagnetic principle, and containing a new compass unit. Marsh-McBirney, Inc. 196

Particle measurement. Bulletin MB 402 describes the company's PI MC particle measurement computer system that interfaces a microscope, television screen, television camera, and computer. System is modular. Millipore Corp. 197

Air pollution control. A 12-page multicolor brochure (Bulletin 300) describes the company's capabilities in air pollution control systems. Fabric collectors, wet scrubbers, and other control equipment are covered. American Air Filter Co., Inc. 198

Graduate programs. The third edition of "Register of Environmental Engineering Graduate Programs" is now obtainable. Dr. Joe Malina, Director of Environmental Health Engineering, 305 Engineering Labs Bldg., University of Texas, Austin, Tex. 78712. (Write direct.)

Polyimide solutions. Brochure A-96100 describes the company's new NR-150 polyimide solutions and binders to produce higher-strength thermosetting plastics with many applications. Room N-24100, Du Pont Co., Wilmington, Del. 19891. (Write direct.)

Noise control. Report by company president delves deeply into many aspects of the subject of noise-level criteria and noise-control engineering

methods. Ask for IAC Bulletin 6.0010.0. Industrial Acoustics Co., 1160 Commerce Ave., Bronx, N.Y. 10462. (Write direct.)

Tire reuse. Booklet describes how to tell when a tire needs replacing, and how it can be turned in for recycling. It also explains the cost and energy-saving benefits of retread tires. Tire Retread Information Bureau, 1343 L St., N.W., Washington, D.C. 20005. (Write direct.)

List of publications. Annual compilation for 1973 of papers and articles by the staff is available. Energy and environmental subjects comprise part of the list. Battelle Memorial Institute, 505 King Ave., Columbus, Ohio 43201. (Write direct.)

Publication list. List of publications contains material covering all aspects of air pollution control technology. Publications Department, Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, Pa. 15213. (Write direct.)

Precipitator principles. Technical paper describes hot-type precipitator for collection of fly ash from low-sulfur coal, with emphasis on sizing parameters, reliability factors, and special design details. Ask for Technical Paper TR-201. Research-Cottrell, Inc. Air Pollution Control Div., Box 750, Bound Brook, N.J. 08805. (Write direct.)

Chemical plants overseas. Booklet describes benefits of multinational chemical companies for the U.S. and for the host countries where overseas plants are located. Manufacturing Chemists Association, 1825 Connecticut Ave., N.W., Washington, D.C. 20009. (Write direct.)

Pesticides. A publication, "The National Pesticide Monitoring Program," is now available as the first comprehensive look at the program for the general public. National Agricultural Chemicals Association, 1155 15th St., N.W., Washington, D.C. 20005. (Write direct.)

Aerator. A 10-page brochure, "Water Pollution Solutions," describes the company's "Oxy-Flo" high-speed floating aerator, capabilities, and the role of aerator in solving water pollution problems. Richards of Rockford, Inc., 6308 Material Ave., Rockford, Ill. 61111. (Write direct.)

Water quality definitions. Report outlines the need for better definitions of water quality. Title is, "Research Needs in Water Quality Criteria, 1972." National Academy of Sciences and National Academy of Engineering, 2101 Constitution Ave., N.W., Washington, D.C. 20418. (Write direct.)

BOOKS

Guide to Water Cleanup: Materials and Methods. Arthur D. Little, Inc. 350 pages. New Boston House, 114 Lowell St., Andover, Mass. 01810. 1974. \$29.95, hard cover.

Represents a first compilation in which important engineering data are provided, as well as solid information about performance, operating specifications, compatibility, power and manpower requirements, and other important data. Also covers state and federal laws and regulations, contingency planning, and many other germane topics.

Solar Energy: Technology and Applications. J. Richard Williams. ix + 120 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1974. \$9.95, hard cover; \$6.95 paper.

A leading expert discusses production-practicability, cost and equipment, comparison with other fuel sources, heating, cooling, electric power generation, and related energy sources. Encompasses the broad spectrum of solar energy research and development.

Against Pollution and Hunger. Alice M. Hilton, Ed. 200 pages. Halsted Press, 605 Third Ave., New York, N.Y. 10016. 1974. \$12.95, hard cover.

Presents papers given at the International Pollution Control Conference sponsored by the Society for Social Responsibility of Science. Contributors share their knowledge and experience in finding a way against pollution and hunger. Many problems are identified, and remedies are suggested for careful exploration. Papers are on physical and chemical aspects of pollution, radiation and human health, genetic damage, and chemical and biological warfare.

Instrumentation in the Power Industry. Vol. 17. Instrument Society of America. 128 pages. Instrument Society of America, P.O. Box 34093P, Pittsburgh, Pa. 15230. 1974. \$12, paper (\$10 to ISA members).

This volume contains 15 papers on present practices and future trends in power industry instrumentation. Topics cover computer applications, air quality monitoring, power plant dynamics, conversion of units to alternate fuels, and cooling tower instrumentation and controls.

Interdisciplinary Environmental Approaches. Albert E. Utton, Daniel H. Henning. 250 pages. Educational Media Press, P.O. Box 1852, Costa Mesa, Calif. 92626. 1974. \$8.95, paper.

The book's objective is to supply theoretical information on environmental studies by relating a comprehensive approach which draws from 20 interrelated academic disciplines. The book deals with environmental approaches and studies by disciplines. It contains the largest collection of environmental theory by disciplines to be found under one cover, and it emphasizes the theme of resource rehabilitation.

Handbook of Marine Environmental Engineering. Frank L. Cross, Jr., Ed. Technomic Publishing Co., Inc., 265 W. State St., Westport, Conn. 06880. 1974. \$35, hard cover.

This reference book deals with various problems in oceans, harbors, channels, rivers, and large lakes. It covers air pollution control, oil and hazardous materials spills, sewage treatment, industrial wastewater, storm water runoff, solid waste, and related topics. Also included are legal considerations, environmental impact statements, occupational safety and health, and an assessment of future trends.

World Directory of Environmental Research Centers. William K. Wilson, Morgan D. Dowd, Phyllis A. Sholtys, Eds. R. R. Bowker, P.O. Box 1807, Ann Arbor, Mich. 48106. 1974. \$19.50.

The directory lists 5300 organizations in some 114 countries throughout the world. Entries are alphabetical according to discipline, such as biology, chemistry, and the like. Categories are further broken down by 30 subheads. All types of environmental research centers—commercial, government, field, and others—are given with names of directors, sizes of staffs, and areas of specific interest.

Energy: Today's Choices, Tomorrow's Opportunities. Anton B. Schmalz, Ed. 301 pages. World Future Society, 4916 St. Elmo Ave., Bethesda, Md. 20014. 1974. \$6.00, paper.

About 71 government officials and energy experts present their views in this book which emphasizes that the

American people will suffer greatly from energy problems unless the rapid expansion of the consumer economy is brought to a halt. An important theme is the "three R's—recycle, reuse, repair." Practical methods of conserving energy are brought out.

It Happened Last Year: Earth Events—1973. James Cornell, Ed. 250 pages. Macmillan Publishing Co., Inc., 866 Third Ave., New York, N.Y. 10022. 1974. \$7.95, hard cover; \$3.95, paper.

This book is the annual report of the Smithsonian Center for Short-Lived Phenomena, compiled from reports by 1600 scientists and 44,000 students in 136 countries on a round-the-clock alert for such events. It covers oil spills, earthquakes, rodent infestations, and many other sudden, not always explainable short-lived events. Contains tear-out cards so that the reader may report phenomena he witnesses.

Working Papers on the Uses of Regional Science Techniques in Environmental Management. Walter Isard, Frank J. Cesario, Eds. 198 pages. Center for Urban Development Research, Cornell University, 726 University Ave., Ithaca, N.Y. 14850. \$4.50.

Contains seven papers which deal with ideas, formulations, and techniques in regional science and environmental management. Economic-environmental analyses are discussed. Models for estimating quantity and responsibility for pollutants are given, and a relationship between long-run urban form and air quality improvement is formulated.

Practical Building of Methane Plants. L. John Fry, 1223 North Nopal St., Santa Barbara, Calif. 93103. 1974. \$12.

Written for operators of small and large farms, homesteads, dairies, and feedlots, canneries, and the like. It is aimed at fostering rural energy independence. Plans and specifications for plant-building are given, and the scum removal problem, a major source of difficulty with methane plants, and solutions to the problem, are discussed. Capital, operational, and labor cost savings are listed. The writer has a great deal of hard, personal experience to back his ideas.

MEETING GUIDE

September 30–October 3 Boston, Mass.

Secondary Fiber Pulping Conference. TAPPI

Contact: S. J. Hayes, TAPPI, 1 Dunwoody Park, Atlanta, Ga. 30341

September 30–October 4 New Orleans, La.

Navy Health and Safety Workshop. Dept. of the Navy

Emphasis on federal occupational safety and health and environmental quality. Write: W. A. Redman, Jr., Navy Environmental Health Center, 3333 Vine St. Cincinnati, Ohio 45220

October 6–11 Denver, Colo.

1974 WPCF Conference. Water Pollution Control Federation

Contact: Robert Canham, WPCF, 3900 Wisconsin Ave., Washington, D.C. 20016

October 7–10 Chicago, Ill.

Pack Expo 1974 Fibre Box Association

Write: FBA, 224 S. Michigan Ave., Chicago, Ill. 60604

October 14–18 Champaign, Ill.

Precipitation Scavenging. Atomic Energy Commission

Write: R. W. Beadle, Physical and Chemical Transport Program, Div. of Biomedical and Environmental Research, AEC, Washington D.C. 20545

October 14–18 McLean, Va.

Workshop on Hydrologic and Aquatic Simulation—Hydrology. Hydrocomp, Inc.

Write: D. L. Hey, Hydrocomp, Inc., 1502 Page Mill Road, Palo Alto, Calif. 94304

October 14–19 Denver, Colo.

Annual Meeting. Association of Engineering Geologists

Write: William Rogers, Tech. Program Chairman, Box 15124, Denver, Colo. 80215

October 15–17 Research Triangle Park, N.C.

Seventeenth Biological Safety Conference. Becton, Dickinson, and Co.

Subjects to be covered include NCI guideline for carcinogens, environmental pollution, and OSHA and EPA regulations for biological labs. Write: L. A. Taylor, B-D Co., P.O. Box 12016, Research Triangle Park, N.C. 27709

October 15–17 Toronto, Canada

The Corrosive World Around Us. National Association of Corrosion Engineers—Canadian Region

Emphasis on how soil, air, and water enter into corrosion situation, applicable to process industries and utility operations. Write: J. R. Alexander, c/o Acres Consulting Services Ltd., 20 Victoria St., Toronto, Ont. M5C1Y1, Canada

October 16–18 Honolulu, Hawaii

American Water Works Association—California Section Conference. Water and Wastewater Equipment Manufacturers Association

Write: WWEMA, 744 Broad St., Rm. 3401, Newark, N.J. 07102

October 19–20 Worcester, Mass.

Energy Sources—'74. The Sierra Club and others

Write: D. C. Blitzer, 784 Memorial Drive, Cambridge, Mass. 02139

October 21–23 Madison, Wis.

Lake Protection and Management. EPA and others

Write: Lake Protection & Management Conference, U. of Wisconsin-Extension, 1815 University Ave., Madison, Wis. 53706

October 21–25 McLean, Va.

Workshop on Hydrologic and Aquatic Simulation—Water Quality. Hydrocomp, Inc.

Write: D. L. Hey, Hydrocomp, Inc., 1502 Page Mill Road, Palo Alto, Calif. 94304

October 21–25 Kansas City, Mo.

Environmental Engineering Meeting. American Society of Civil Engineers

Write: ASCE, 345 E. 47 St., New York, N.Y. 10017

October 22–23 Pittsburgh, Pa.

Executive Management Seminar. Industrial Health Foundation

Emphasis is on occupational health and safety regulations and their economic impact. Write: Industrial Health Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232

October 22–24 Louisville, Ky.

Coal and the Environment Exposition. The National Coal Association and others

Contact: M. B. Wolf, P.O. Box 17413, Dulles International Airport, Washington, D.C. 20041

October 27–29 Mexico City, Mexico

International Patterns of Engineering Management—A Constructive Analysis. American Society of Mechanical Engineers

Includes natural resource development and environmental matters. Contact: C. Garvin, ASME, 345 E. 47th St., New York, N.Y. 10017

October 27–31 Washington, D.C.

Annual Conference. Atomic Industrial Forum, Inc.

Emphasizes the challenges to industry, government, and the public in nuclear electric generation. Write: Conference registrar, Atomic Industrial Forum, Inc., 475 Park Avenue South, New York, N.Y. 10016

November 1 Washington, D.C.

Environment and Safety Briefing Session. The Bureau of National Affairs, Inc.

Write: F. B. Tagg, The Bureau of National Affairs, Inc., 1231 25th St. N.W., Washington, D.C. 20037

November 6–7 East Lansing, Mich.

Environmental and Economic Impact of Packaging in the Food Industry. Michigan State University

Write: J. R. Kirk, Dept. of Food Science and Human Nutrition, School of Packaging and Continuing Education, Kellogg Center, Michigan State University, East Lansing, Mich. 48824

November 12–14 Santa Barbara, Calif.

Report on Los Angeles Reactive Pollutant Program. EPA and others

Write: Coordinating Research Council, 30 Rockefeller Plaza, New York, N.Y. 10020

November 13–14 Indianapolis, Ind.

Annual Purdue Air Quality Conference. Indiana University Purdue University at Indianapolis

Emphasis is on major current air quality and fuel problems. Contact: R. E. Johnson, IUPUI, 1201 E. 38th St., Indianapolis, Ind. 46205

November 13–15 Chapel Hill, N.C.

Land Use and Transportation Planning and Air Quality Maintenance. EPA, DOT, and Triangle Universities

Attendance limited to 125. Contact: D. Powell, TUCAP, P.O. Box 2284, Chapel Hill, N.C. 27514

November 13–15 College Corner, Ohio

Second Conference on Energy and Environment. American Institute of Chemical Engineers and others

Contact: D. E. Earley, 4831 Haplin Drive, Dayton, Ohio 45439

November 17–21 New York, N.Y.

Winter Annual Meeting. American Society of Mechanical Engineers

Includes environmental and energy discussions. Write: M. Jones, ASME, 345 E. 47th St., New York, N.Y. 10017

November 18–23 London, England

Biennial Public Works and Municipal Services Exhibition. British government and others

Write: The Municipal Agency Ltd., 178/202 Great Portland St., London W1N 6NH, England

(Continued on page 955)

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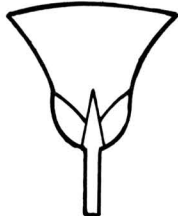
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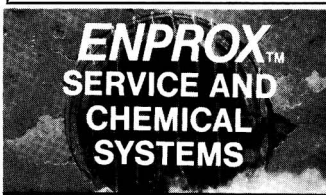


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Dohrmann	876
Fred Schott Associates	
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Gaynor & Ducas Advertising	
Kontes Glass Company	889
Aitkin-Kynett Co., Inc.	
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Pallace Incorporated	
Philips Electronic Instruments	878
J&M Condon, Inc.	
Plenum Pub. Corp.	906
Plenum Publishing Corp.	

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Langler-Stevens, Incorp.	
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J. M. Ferrazza Associates Inc.	
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Campbell-Mithun, Inc.	
Western Precipitation	881
Reeds & Farris	

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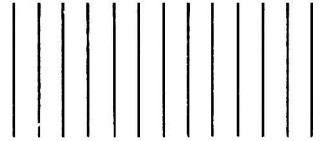
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43	44	45	46	47	48	49	50	51	52	53	54	55	56
57	58	59	60	61	62	63	64	65	66	67	68	69	70
71	72	73	74	75	76	77	78	79	80	81	82	83	84

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115	116	117	118	119	120	121	122	123	124	125	126	127	128
129	130	131	132	133	134	135	136	137	138	139	140	141	142
143	144	145	146	147	148	149	150	151	152	153	154	155	156
157	158	159	160	161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180	181	182	183	184
185	186	187	188	189	190	191	192	193	194	195	196	197	198

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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	61	62	63	64	65	66	67	68	69	70
71	72	73	74	75	76	77	78	79	80	81	82	83	84

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115	116	117	118	119	120	121	122	123	124	125	126	127	128
129	130	131	132	133	134	135	136	137	138	139	140	141	142
143	144	145	146	147	148	149	150	151	152	153	154	155	156
157	158	159	160	161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180	181	182	183	184
185	186	187	188	189	190	191	192	193	194	195	196	197	198

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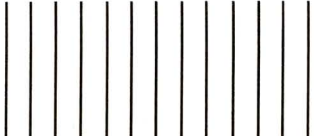
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