# Environmental
# Science & Technology

✓JUNE 1974

Controls at Four Corners 516

# 67th APCA ANNUAL MEETING

June 9–13, 1974 Denver, Colorado

# EXHIBITORS

## New DSL Probe from CEA Instruments Extends Use of U2-DS into the Stack

The high level DSL probe is an accessory for the CEA Instruments Model U2-DS Ultra Portable $SO_2$ Analyzer. It extends the normal maximum range of the U2-DS, which is 0–20 ppm in six steps (0–0.5, 0–1, 0–2, 0–5, 0–10, and 0–20) by a factor of 200. This results in a maximum range of 0–4000 ppm down to 0–100 ppm full scale in six steps, allowing fast, direct measurements of very high $SO_2$ levels as found in stationary sources, process systems, etc.

**Booth 600 See Advertisement on Page 512** **Circle 38**

## RAC Introduces New Instruments for Sampling, Monitoring, and Calibrating

Research Appliance Company (RAC) is presenting a variety of new and improved products for sampling/monitoring pollutants in ambient air and process emissions at the 67th APCA annual meeting. New designs include (1) a Transmisometer that evaluates combustion and process emissions by degree of opacity, (2) a computer-controlled Automatic Stack Monitor that measures particulate mass in stack gas streams by beta gage radiation, (3) a lightweight two-module sample case for RAC Staksamplr systems, (4) a 4-Gas Sampler equipped with four separate pumps and bubblers, and (5) a portable Calibrator that features ±1% flow measurement accuracy for calibrating ambient air monitoring instruments.

**Booth 325 See Advertisement on Page 490** **Circle 36**

## EG&G High-Precision Dew Point and Visibility Monitoring Instruments

Widely used for:

- Air Pollution Studies
- Meteorological Monitoring
- Nuclear Plant Siting Studies
- Nuclear Plant Monitoring

Don't miss EG&G's Model 207 Forward Scatter (Visibility) Meter, and the Model 110 Weather Station featured at the APCA Show. Also on display—the NEW Model 440 Dew Point Hygrometer, a high-precision instrument designed and priced for industrial use.

**Booth 616 See Advertisement on Page 528** **Circle 29**

## Du Pont Source Monitoring Systems for $SO_2$, $NO_2$, $NO_x$, $H_2S$, $Cl_2$

Proved in extensive field use, the Du Pont systems provide reliable measurement of stack gas emissions. Complete, with sample systems, ready for installation.

Available for both continuous or sequential sampling; plus $H_2S/SO_2$ ratio analyzer for Claus sulfur recovery process control.

Analyzer system also available for monitoring low levels of phenols in wastewater.

Du Pont Co., Instrument Products Division
Wilmington, DE 19898

**Booth 508** **Circle 33**

## Get the Facts About Thermo Electron's New Instruments at Booth 316

- New Model 14D Dual Chamber Single-Tube Ambient Air Chemiluminescent NO–$NO_x$ Analyzer
- New Model 43 Pulsed Fluorescent Ambient Air $SO_2$ Analyzer
- New Model 8A Portable Chemiluminescent NO Analyzer
- New Model 101 Calibrator for Ambient Air Analyzers
- Model 40 Pulsed Fluorescent $SO_2$ Stack Monitor
- Model 12A Ultrasensitive Chemiluminescent NO–$NO_x$ Analyzer for Laboratory Use.

Thermo Electron Corp.
Environmental Instruments Div.
85 First Ave., Waltham, MA 02154
Phone: 617-890-8700

**Booth 316** **Circle 35**

## High Purity, Hydrogen/Oxygen Generators

Featured at Teledyne Isotopes' exhibit are Electra Cell gas generators designed specifically for the support of single or multiple gas analyzer installations and for general laboratory use. The HG series, rated at 500, 750, or 1000 sccm of high-purity hydrogen, can also be ordered as combination units, producing oxygen at one half the hydrogen capacity. Accessory equipment is available for further reduction of moisture and impurities.

Teledyne Isotopes
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Phone: 201-664-7070 Telex: 134-474

**Booth 620** **Circle 37**

## Arthur H. Thomas Is More Than a Lab Supply House

Stack samplers, atmospheric particle samplers, and personnel monitors are not lab items. That's why Thomas is at APCA. Pleased and proud as we are to serve as your source for laboratory equipment and supplies, we'd like to show you how we've branched out.

We're showing our Pollution Trace Oven and other lab items also. But mainly, we're trying to show that you now have a good single source for both lab and on-site pollution test equipment.

**Booth 213** **Circle 13**

# Credentials

**Philips PW9700 $SO_2$ Monitor**
Gives the highest correlation coefficient (0.933) with West Gaeke, the EPA reference method. Determined by field evaluation of air pollution monitors conducted under EPA Contract No. CPA 70-101.*

**Philips PW9700 $SO_2$ Monitor**
The only $SO_2$ monitor for remote and local siting. Long term unattended operation provides for low operating costs and manpower requirements. Requires maintenance only 4 times a year. Every other $SO_2$ monitor requires daily attention.

**Philips PW9700 $SO_2$ Monitor**
Its four year record of performance and reliability is unparalleled.

**Philips PW9700 $SO_2$ Monitor**
The most widely used $SO_2$ monitor in the U.S. and worldwide.

*Field Evaluation of New Air Pollution Monitoring Systems, Final Report, May 8, 1970 through May 8, 1972.

Call Philips today. Ask for the Product Manager, Environmental Quality Monitoring, 914-664-4500, he'll be glad to describe the PW9700 and our monitoring systems.

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# Environmental
Science & Technology

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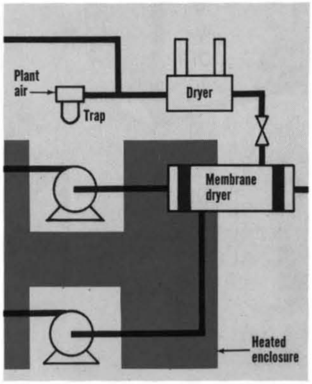

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### Special report

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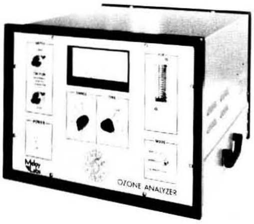
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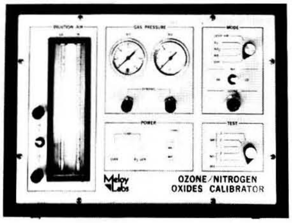
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SO2 CALIBRATION SYSTEM
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For author's guide and editorial policy, see this issue, page 549, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*

Readers may have noticed recent changes in grades of paper on which this and other ACS journals are printed. The changes are a result of the general paper shortage, and ACS regrets any possible inconvenience. The journals will continue to be printed on the best quality paper available in sufficient quantity for press runs.

## Airing air cleanup

Discussion is good. It always has been. It 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 Air Pollution Control Association meet at another annual conclave to discuss cleanup.

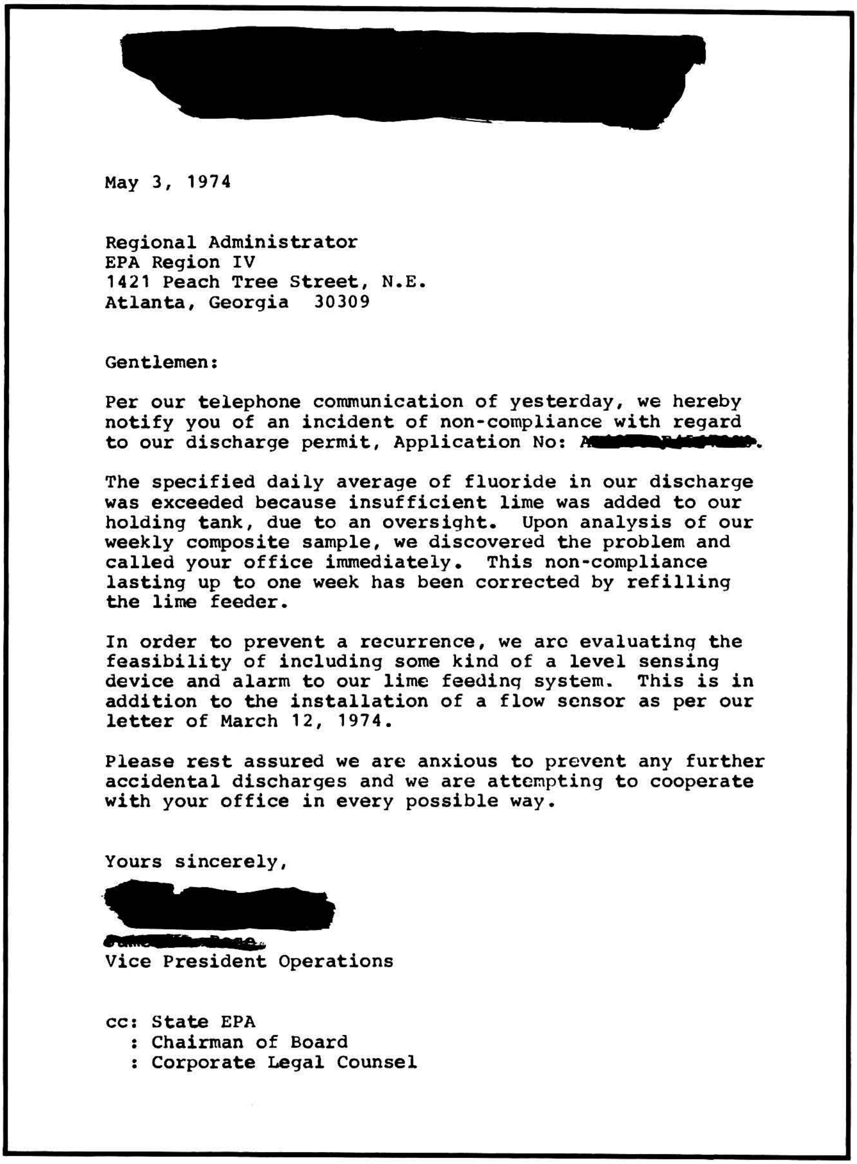
*ES&T*'s William Forester points out in this month's special report that state air pollution control officials now are a bit more doubtful than earlier that deadlines in the Clean Air Act can be achieved within the time specified in the law. This issue also includes information on other air cleanup subjects—monitoring, fabric filters, one utility's experience with stack gas cleanup equipment, and another's with fuel cleaning prior to its burning.

But what does the most recent indicator reveal about cleanup progress? Well, good news on such progress comes from Bermuda—the site of this year's annual conclave of the IGCI, the trade association of industrial air pollution control equipment manufacturers. On the specific subject of compliance in $SO_2$ control from fuel burning sources, EPA's Richard Wilson, director of the division of stationary source enforcement, referred to the fact that 20,000 major facilities account for 85% of all particulate matter and $SO_2$ emissions. Half (or 50%) are in compliance today, up from 30% in July 1973. All but 3000 sources are on approved compliance schedules and many of the remaining 3000 may be under such schedules as early as next month. At the same time there are about 111 so-called, noncomplying utility plants operated by 44 companies; requests for their compliance schedules also have been made.

To be sure, there is much more than meets the eye to these environmental conclaves, or any others for that matter. There is much behind-the-scene, daily endeavor by many devoted people. And well there should be. But to those self-appointed critics who would point out that little in the way of new practices or operating procedures results even after lengthy, often animated, discussion, we can only submit that clearing the air is as necessary as the objective—cleaning the air.

Stanton Miller

# The "dear EPA" letter.



[redacted]

May 3, 1974

Regional Administrator
EPA Region IV
1421 Peach Tree Street, N.E.
Atlanta, Georgia 30309

Gentlemen:

Per our telephone communication of yesterday, we hereby notify you of an incident of non-compliance with regard to our discharge permit, Application No: [redacted].

The specified daily average of fluoride in our discharge was exceeded because insufficient lime was added to our holding tank, due to an oversight. Upon analysis of our weekly composite sample, we discovered the problem and called your office immediately. This non-compliance lasting up to one week has been corrected by refilling the lime feeder.

In order to prevent a recurrence, we are evaluating the feasibility of including some kind of a level sensing device and alarm to our lime feeding system. This is in addition to the installation of a flow sensor as per our letter of March 12, 1974.

Please rest assured we are anxious to prevent any further accidental discharges and we are attempting to cooperate with your office in every possible way.

Yours sincerely,

[redacted]

[redacted]
Vice President Operations

cc: State EPA
: Chairman of Board
: Corporate Legal Counsel

*Your discharge permit calls for composite sampling, but composite sampling doesn't keep you from polluting, it only shows if you have or haven't. The way to be sure you stay within permit levels is by continuous monitoring of your discharge — so you can do something about setting things right the moment something goes wrong. If you would like to know about our continuous on-line monitors for ammonia, cadmium, chlorine, copper, cyanide, lead, nitrate, and other inorganic species — write to our Monitor Division. It beats writing the EPA!*

**ORION RESEARCH**
**380 Putnam Avenue Cambridge, MA 02139**

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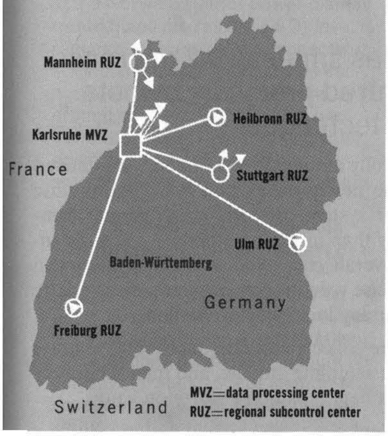
# CURRENTS

## INTERNATIONAL

**What officials call "the first overall, supraregional, air pollution monitoring network"** presently is under construction at Baden-Wurttemberg, in Southwest Germany. Being set up under contract with the Siemens Co., the monitoring stations automatically will register the most important meteorolgical data and pollution levels and transmit them by remote-control equipment to a regional subcontrol center in Mannheim. There they are to be analyzed. Presently, three major stations are being set up within the framework of the smog-warning system for the highly industrialized area of Heidelberg-Mannheim-Ludwigshafen-Frankenthal. A main control center at Karlsruhe, plus other subcontrol centers are planned for a later stage.

iemens' air monitoring network



**The U.S.—U.S.S.R. cooperative group** studying the influence of evironmental change on the climate will hold its first meeting this month in Leningrad. The group, Working Group VIII, is one of 11 established under an Environmental Protection Agreement in 1972. The agreement provides for cooperative studies ranging from air pollution to legal and administrative matters.

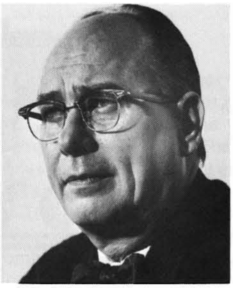
## WASHINGTON

**The Environmental Protection Agency has undergone some reorganization.** The former Office of Air and Water Programs has been divided into two separate offices, and the Office of Hazardous Materials Control has been abolished. The realignment establishes new offices of Water and Hazardous Materials and Air and Waste Management. James L. Agee, EPA Region 10 administrator, has been named acting assistant administrator for Water and Hazardous Materials. Roger Strelow will continue as acting assistant administrator for Air and Waste Management. In other agency news, Stanley M. Greenfield, former assistant administrator for Research and Development, has left to join a private firm.

**Maximum noise levels for protecting the public against hearing loss,** annoyance, and activity interference have been set by the EPA. The agency identifies a 24-hr exposure level of 70 decibels (db) as necessary to prevent measurable hearing loss over a lifetime. Likewise, levels of 55 db outside and 45 db inside are set as necessary to prevent activity interference and annoyance.

**The EPA has further cracked down** on uncooperative manufacturers and distributors dealing in vinyl chloride products. The agency has released the brand names of 20 pesticide products whose registration statements indicate they contain the chemical as a propellant. In addition, it has published the names of 10 manufacturers and distributors who refused to permit release of their brand name products. Vinyl chloride is suspected to cause a rare form of liver cancer, called angiosarcoma, which has occurred in 12 workers engaged in production of the chemical or its conversion to polyvinyl chloride. The EPA has asked all manufacturers and distributors to recall, voluntarily, stocks of their products. Thus far, most have been willing to do so.

**The U.S. still does not know whether its water quality is getting better or worse.** Not enough data have been collected to provide a quantitative answer to this question, according to V. E. McKelvey, director of the U.S. Geological Survey. In a recent speech, he pointed out that USGS and Council on Environmental Quality studies reveal that only 142 stream-quality stations nationwide—70% are in the Northwest—have records that meet trend-studies requirements. In a separate speech, McKelvey noted that the total energy potential for the Appalachian area remains quite large, but that production of its energy resources entails difficult environmental problems that will have to be overcome if these resources are to become usable.

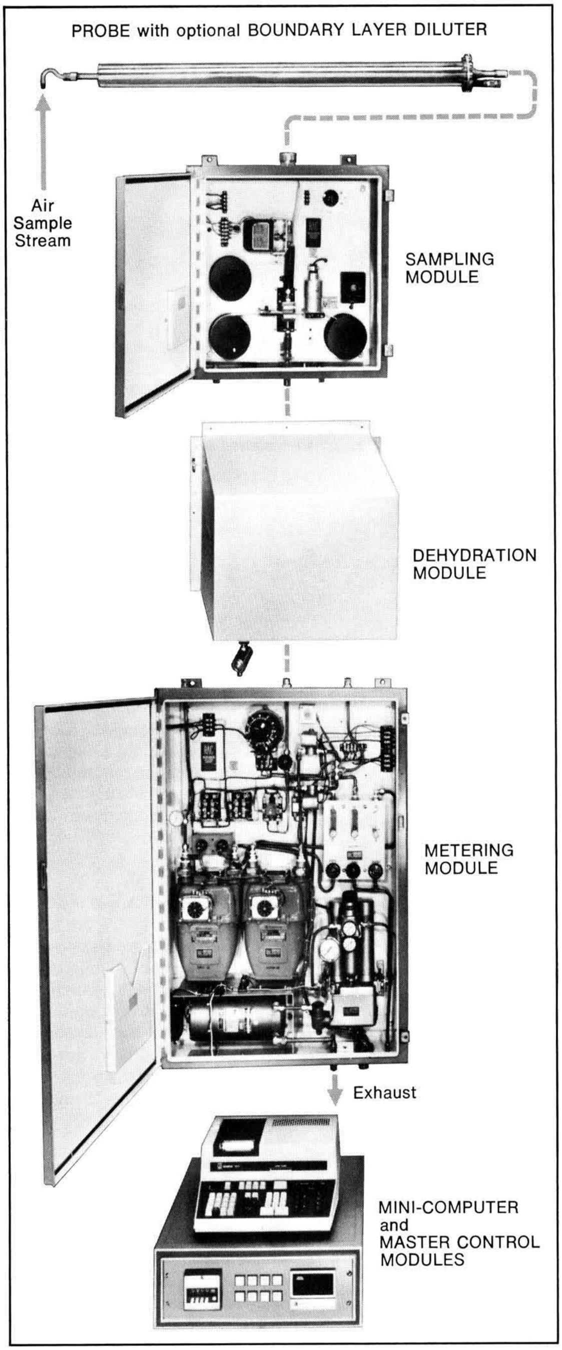

*USGS director McKelvey*

**Proponents of dumping garbage and other wastes on the deep ocean floor may have second thoughts.** Oceanographers have found that while such waste may readily be consumed by active organisms in shallow water, it may simply accumulate in deep water because of a biologically slower pace of life.

**The Department of Labor and the EPA have set up a joint program to train welfare recipients** for permanent environmental control jobs. A $1 million pilot project will be undertaken in Baltimore, Baton Rouge, Dallas, Denver, and on a statewide basis in South Carolina. It is hoped this pilot project will set the pattern for a nationwide federal, state and local program.

## STATES

**St. Louis, Mo., got its first of 25 remote air-monitoring stations** in its botanical garden, as part of EPA's comprehensive regional air pollution study (RAPS) in the greater St. Louis area (*ES&T*, July 1973, p 598). Spanning five years and costing $22 million, the program aims to gather sufficient information on air pollutants to enable planners, U.S. and abroad, to develop more effective plans in combating air pollution. Covering both Missouri and Illinois portions of the St. Louis area, the stations will be equipped with a minicomputer, electronic air monitoring



Fully automated, computerized

# RAC Automatic Stack Monitor

## samples...measures...records particulates in stack emissions

### Particles as small as 0.2 microns are measured precisely by beta radiation technique

Designed for fully automatic, continuous, unattended operation, the newly-developed RAC Automatic Stack Monitor system provides much greater sampling accuracy than manual methods . . . at substantially lower overall cost. And it is the *only* system that takes precise volumetric measurements to assure optimum accuracy in sample evaluation.

Particulates are collected on filter tapes (600 samples per roll) in the sampling module, and then accurately measured by a beta radiation absorption gauge.

All system calculations are made automatically by a mini-computer that is interlocked with the master control module. Results are recorded on a tape printout.

The RAC Automatic Stack Monitor operates in stacks with temperatures up to 1000°F. When high temperature, humidity, or particulate concentrations are involved, RAC offers a unique (and exclusive) *boundary layer diluter* assembly. This optional component preconditions the sample stream with dry instrument air before it enters the sampling module.

The system's metering, master control, and mini-computer modules can be located up to 250 feet away from the stack-mounted sampling module. The probe and optional diluter (if used) are permanently installed in the stack.

*Write for BULLETIN 2412 for full details.*

CIRCLE 26 ON READER SERVICE CARD

**STACK SAMPLING SEMINARS (4th Year)**
RAC sponsors a series of 2-day technical how-to seminars on stack sampling parameters and procedures (EPA method). **Write for descriptive folder.** CIRCLE 25 ON READER SERVICE CARD

RAC

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***Environmental Instruments / Laboratory Products***

equipment, and meteorological instruments, and will be built and operated by Rockwell International Corp.

**At a Connecticut electric power plant, a new $SO_2$ abatement process** is undergoing its first commercial test demonstration. Developed and operated by Stauffer Chemical, the regenerative process is said to yield high-purity sulfur that can be sold commercially. A slip-stream of raw flue gas from a 165-mW oil-fired boiler at the Norwalk Harbor power plant is treated, and the resulting $SO_2$ level is reduced to levels below Connecticut state standards. Capital cost is estimated at about $35 per mW and operating cost at about 1.5 mills per kWh. Start-up in February and shutdown in April have resulted in smooth demonstration of the system.

**About 3000 workers in Minnesota were saved from unemployment** by a temporary court order which reopened an iron ore manufacturing plant closed down four days previously because of pollution. Reserve Mining Co.'s taconite processing plant at Silver Bay provides 15% of the iron ore produced in the U.S. It was ordered shut down by a federal judge on the ground that it allegedly discharges asbestos fibers into the air and nearby Lake Superior. This ruling came as a result of suits filed by the federal government, the states of Michigan, Wisconsin, and Minnesota, charging that the asbestos wastes from taconite can be carcinogenic. A full circuit court hearing was set for May 15.

**New Jersey's Department of Environmental Protection approved the Tocks Dam Project,** following more than a decade of environmental controversy. Of the four states—Pennsylvania, New York, Delaware, New Jersey—which were to benefit from the dam, N.J. had been the only one actively opposed to the construction of the $325 million dam. Its main objection had been the possible destruction of one of the last whitewater rivers on the East Coast by too much commercial exploitation. The final decision to construct the dam across the upper Delaware River will be made jointly by the four states after public hearings which commenced in April.

**Resource recovery is being tested at the District of Columbia's** solid waste reduction center. The National Center for Resource Recovery (NCRR) is using the district's facility and shredder to identify and evaluate various processes to separate metals and glass from shredded refuse. They are also exploring the air-classified light fraction as a source of energy. Equipment—air classifier, trommel, screens, magnetic separator, rising current separator—is supplied by the manufacturers. The project, which began last month, will supply the experience and data for a full-scale recovery system to be built in New Orleans later this year. New Orleans has called for bids for a 650-ton-per-day resource recovery facility to be built according to NCRR specifications.

**Flower Mound New Town, Tex., was opened and dedicated** April 20. Claiming to be an environmentally planned town, the first indication will be a tertiary sewage treatment plant targeted for dedication in early summer. The plant, located on a 25-acre site, will initially treat 700,000 gal. of effluent per day, or normal service for 6000 persons. As the population expands, the plant will increase its capacity to 7.5 million gal. to serve 50,000 persons. Total cost of plant and lines is approximately $1.75 million—75% financed by federal grants from the EPA and the Department of Housing and Urban Development, 25% financed through long-term bonds issued by the utility district.

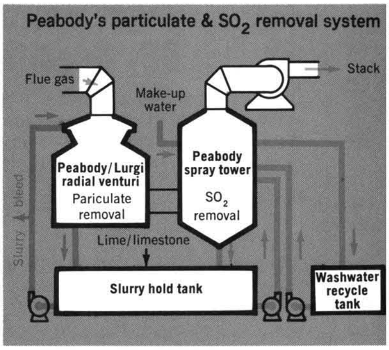
## MONITORING

**A continuous automatic analyzer for high turbidities and colors** in water samples was developed by the Hach Chemical Co. This general-purpose instrument accommodates a troublesome problem in the colorimetric analysis of such samples. Capabilities for color and turbidity compensation, and for maintenance of clean, uniform sample cells for optical color measurement, were required. The system chosen consists of two sample cells, a single light source of selected wavelength, and a single photocell, operated in a sequential mode.

**A soft X-ray spectrographic technique** reveals both the amount and forms of sulfur (S) in coal. The 15-min technique developed at The Pennsylvania State University excites S atoms so that they emit their own X-rays. These X-rays of S tell whether the S is organic, pyritic, sulfate, or any combination of these, by characteristic peaks on a graph. The Penn State technique was originally developed to determine the quartz content of coal dust.

## TECHNOLOGY

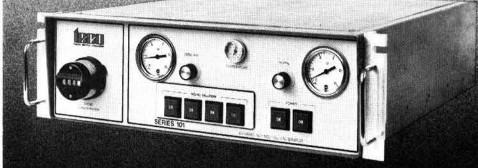
**A full-scale $SO_2$ removal system,** using Peabody radial venturi and high-velocity spray tower designs, is under construction at Detroit Edison's St. Clair Station (170-MW Unit #6). The system, designed and built by Peabody Engineered Systems (Peabody Galion Corp.) will handle 500,000 acfm of flue gas from a boiler firing 4% sulfur coal. During pilot plant tests, the scrubber system removed 90% of $SO_2$ on the average; outlet dust loading averaged 0.006 grain/scf; and scale formation was generally absent. In the full-scale system, maximum $SO_2$ outlet should be 300 ppm, after $SO_2$ absorption with a limestone slurry.



**Commercial sulfuric acid produced from $SO_2$ emission control** at an electric power system was the subject of a joint TVA/EPA study. This study was one of a series designed to furnish more information about economic feasibility of various

# New Precision Calibrator for Ambient Air Analyzers

Thermo Electron's new Model 101 is a step ahead in calibration of ambient air level analyzers. It uses a new gas titration method to calibrate $O_3$, NO, and $NO_2$, and checks linearity as well. The Model 101 is truly a precision calibrator for precision instruments. Write today for more information.



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Electron
CORPORATION

**Environmental Instruments Division**
**85 First Avenue, Waltham, Mass. 02154 / (617) 890-8700**

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# New, Portable NO Chemiluminescent Gas Analyzer

Thermo Electron introduces its new Model 8A portable NO Chemiluminescent Analyzer. The Model 8A uses a high sensitivity photo detector to monitor the chemiluminescent reaction of NO and $O_3$, and provides an internal sample pump and ozone generator for single package operation.

Ranges up to 2000 ppm, accuracy and linearity to ± 2%, and weight of only 25 lbs. makes the Model 8A the ideal instrument for taking short-term samples at different locations, or from vehicles. Write today for more information.

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**Environmental Instruments Division**
**85 First Avenue, Waltham, Mass. 02154 / (617) 890-8700**

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# Never Before $SO_2$ Specific

Direct, clean, and specific. That's the way you measure $SO_2$ stack emissions with the new state-of-the-art Model 40 Pulsed Fluorescent Analyzer from Thermo Electron.

No flames, consumable reactants, or hazardous bottled gases are required. The Model 40 has 5 full scale ranges from 0.5 to 5000 ppm with precision to 0.5%. It demonstrates linear response through the full range, excellent stability, and freedom from interference. Never before has measurement been so specific. Pulse us for details.

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**Environmental Instruments Division**
**85 First Avenue, Waltham, Mass. 02154 / (617) 890-8700**

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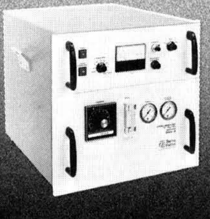
# New Ambient Air Chemiluminescent NO-$NO_X$ Analyzer

Two chambers, one tube, that's the best way to measure ambient air concentrations of NO-$NO_X$ with Thermo Electron's new Model 14D.

The new unit is a sensitive, accurate, interference-free analyzer with unexcelled capability to measure low NO-$NO_X$ concentrations. Ranges vary from 0-50 ppb, to 0-10 ppm, and are linear throughout. Write today for details.



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**Environmental Instruments Division**
**85 First Avenue, Waltham, Mass. 02154 / (617) 890-8700**

CIRCLE 45 ON READER SERVICE CARD

air pollution control processes. The study was based on the assumption that the $SO_2$ would be marketed through existing sulfuric acid manufacturers. The computer model developed for the study can be expanded to include other U.S. electric systems, according to TVA.

**A new polymeric adsorbent decolorizes bleach plant effluents** from kraft paper mills. The single-step procedure was developed by the Rohm and Haas Co. No additional chemicals are needed to regenerate the adsorbent which is marketed under the name "Amberlite XAD-8." Color is eluted from the adsorbent with weak wash from a lime and mud-washing step; the weak wash is then recycled to dissolve smelt from the caustic recovery boiler, where color bodies are consumed without creating another disposal problem.

**A "Sonozone" wastewater treatment plant at Indiantown, Fla.,** was dedicated last month. Using sonic energy and ozone, the Sonozone system "rapidly and completely" inactivates pathogenic viruses, destroys harmful bacteria, and oxygenates surrounding waters. The world's first fully operational, community-sized Sonozone plant will treat the municipal waste of Indiantown, whose population is about 4500. The plant was designed and built by TII (Telecommunications Industries, Inc., Copiague, N.Y.) with the assistance of Notre Dame College of Engineering and Lobund Laboratory.

**Incineration with stack scrubbing and elimination of water effluent** was achieved at two plants at the Fort Lauderdale (Fla.) Refuse Disposal Site. The scrubber system was designed by Burt Reilly of Greenleaf-Teleca (Miami, Fla.), and assembled from component parts by Apgar-Markham (Miami) and Plibrico (Chicago). Smoke is moisturized in a series of water trays, made into sludge, and eventually disposed of in landfills. Water is cleaned with alum, lime-activated carbon, and polymer, and largely recycled to the plants. The first incinerator, built by Nichols Research & Engineering, was retrofitted with the stack gas cleanup system while the second, built by Caldwell & Scott, incorporated the scrubber during construction.

## INDUSTRY

**Columbus Municipal Light (CML), in Ohio, has begun burning 3.5% sulfur coal** on weekends in apparent violation of federal and state clean air standards. CML says that the coal, burned in a 12.5-MW boiler, will not raise sulfur content in Columbus' air above ambient air quality standards. Both the federal and Ohio EPA's rejected CML's arguments recently, with federal appeals court backing. The Ohio EPA might take "some action" in the matter. CML is paying \$32/ton for low-sulfur coal; higher-sulfur Ohio coal is obtainable at \$13.50–14/ton.

**Jack O'Brien, a vice-president of Consolidation Coal Co.** (Consol), said that a workable $SO_2$ removal method is important for most Pennsylvania and West Virginia coal, which is high-sulfur. O'Brien also asked whether this $SO_2$ removal might better be accomplished by a means alternative to scrubbing. David Fyock, director of resources and environmental quality for Pennsylvania Electric Co. (Penelec), said that scrubbing is not demonstrated, and that alternative means must be employed for now. Fyock also said that no new scrubbers should be installed until those now installed are proved up and "debugged."

**The National Asphalt Pavement Association (NAPA) sued the EPA** to overturn EPA's promulgated standard of 0.04 g/dscf emission limits for new and substantially modified asphalt plants. Contending that achievability and compliance are impossible, NAPA charged EPA with being "arbitrary" and "capricious," and with "abuse of discretion," and that EPA violated its statutory authority. NAPA also argued that enforcement will deprive asphalt concrete makers of their property without due process of law, and that EPA violated the Clean Air Act by reducing productivity without corresponding public health and welfare benefits.

**The National Association of Recycling Industries (NARI)** initiated some actions in its campaign to halt railroad freight rate "hikes" until basic transportation rates on recyclables are made "reasonable and non-discriminatory." NARI filed briefs with the Interstate Commerce Commission (ICC) attacking the ICC's "apathy regarding legislative and court orders calling for 'complete investigations' and 'appropriate environmental impact studies.' " NARI contended that the ICC "cannot lawfully . . . . approve any further rate increases until it prepares an adequate environmental impact statement and conducts a proper hearing." NARI noted that ICC wanted to hold hearings after rate increases took effect.

*3 M Co.'s Ling*

**Joseph Ling, director of environmental engineering and pollution control** at the 3M Co., said that Congress and the administration should create a National Environmental Commission (NEC). The NEC's mission would be to develop a national environmental information system, and to take over the standards-setting function from EPA. "Congress did not have an organized environmental information system to provide adequate data when it drew up the Federal Water Pollution Control Act Amendments of 1972," Ling said. Thus, Congress "ordered 'zero discharge' just to made sure" no environmental harm would be done. Ling calls for management based on socio-economic, as well as physical and natural sciences.

**Union Carbide Corp. (UC) is working with EPA** on a two-year study aimed at developing a wastewater treatment system which would recycle petrochemical wastewater at the UC Caribe, Inc., plant at Ponce, P.R. The first step will be a 5-gpm pilot system to be built and tested at UC's technical center, South Charleston, W.Va. Final installation at Ponce, P.R., was decided upon because a sophisticated wastewater facility is already there, and because the area is arid.


ECOLYZER
patents pending
BATTERY TEST
ZERO CAL
ZERO
OFF ON
model 2100
INTAKE
RECORDER
CAUTION
do not connect
to pressure tank


ECOLYZER
CARBON MONOXIDE MONITOR
MODEL 3100

# INTERVIEW

# McKennon on Dow's ECS business

**How did the environmental control systems (ECS) come about?** We first became interested in this area because of the Dow experience in using water-soluble polymers for liquid/solid separation. These polymers are now widely used in wastewater treatment in municipal sewage plants. Dow, perhaps more than any other company, introduced that kind of technology to the municipal wastewater treatment industry; we continue to be a major factor in that market today.

Our ECS business has a marketing organization that sells these flocculants to both municipal and industrial customers. Since that beginning, ECS has evolved to the point where we now offer a wide range of products and services in the environmental control area.

**What does ECS do, specifically?** I've already mentioned the polymers we sell. Our product line also includes inorganic coagulants and some environmental enclosures. Our various service groups and subsidiaries supply customers with help in sophisticated chemical analysis, conceptual and process engineering for environmental control projects, environmental health and industrial hygiene work, modeling and evaluation of receiving waters, and similar activities.

I'd also like to comment on the things we don't do. First off, ECS is not in the equipment business at all. We have developed some good instrument packages, but have elected to license those to companies in that business. Second, our engineering activities are pointed toward work on complex industrial waste problems or on advanced techniques for municipal treatment. As a result, we don't often compete with consulting engineering companies. In fact, such firms are among our best customers since our services can often be used to reinforce their own capabilities.

## MANUFACTURING CONTROLS

**You mentioned Dow's internal environmental control program. What's its magnitude and how is it organized?** We divide that responsibility into two parts. First, there is the environmental impact of our manufacturing operations. Responsibility here rests squarely with our line production management who are charged with meeting or bettering all applicable regulations and guidelines. We have made some major expenditures in this area. In the past three years Dow has completed 1129 pollution abatement projects in our U.S. plants, at a cost of $53.4 million. Substantial additional expenditures have also been made at Dow plants outside the U.S.

The second part concerns what we call "product stewardship," and centers around the environmental impact resulting from shipment, use, and disposal of our products. Each of Dow's businesses has product stewardship responsibility for the product it sells. We are committed to exercising responsible care for our products both during our manufacture and later in their use by our customers. This means assessing the environmental impact of the products and then taking appropriate steps to protect employee and public health, and the environment as a whole. In addition to safe production and judicious customer use, it means we have a continuous concern for the ultimate disposal of our products in the environment. It is the experience gained from programs like these which provides the basis for our ECS business.

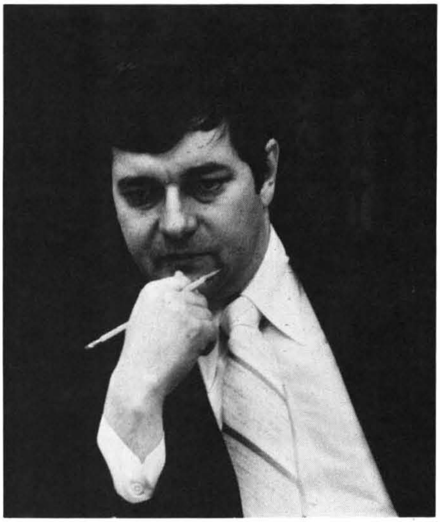
## BREAKDOWN

**Can you be more specific about the service groups in ECS?** Sure. I'll briefly describe each service group and its activities. Dow Environmental Services takes our waste treatment and disposal technology and experience and uses it to develop facilities for our customers. The problems we get are usually tough ones that don't lend themselves to "garden-variety" solutions.

Hydroscience, Inc. is a recent acquisition which operates as a wholly owned subsidiary. Hydroscience provides environmental process design expertise to industrial clients and also does modeling and evaluation of the impact of pollutants on natural water systems such as lakes, estuaries and rivers.

Interpretive Analytical Services (IAS) uses very sophisticated analytical methods and equipment—electron microprobe, neutron activation analysis, gas chromatography-mass spectrometry, and other analytical chemistry techniques which involve

*Keith R. McKennon is business manager for the Dow Chemical's Environmental Control Systems business, one of the company's more than 30 businesses. McKennon tells* ES&T's *Stan Miller that the ECS business activity was formed in the mid-1960's, turned a profit in 1970, and now involves 140 people. Dow's ECS has performed work for more than 150 other major industries in the U.S. Last year ECS sales hit $9 million, up from $7 million in 1972; sales for 1974 are projected at $11–13 million.*



complicated and expensive equipment to do specialized analytical work for our clients.

Dow Environmental Health Services, started in 1971, is essentially an outgrowth of the Occupational Safety and Health Act. We saw a need for environmental health programs in many companies that do not have these capabilities in-house. We felt Dow has a big advantage in providing this service in that Dow has at one location (Midland, Mich.) a wide variety of the scientific disciplines needed to do this job effectively. There are literally hundreds of professionals on tap whose skills can be applied to any environmental health project.

We've been involved in some interesting work; for example, our engineers were responsible for testing and certifying the integrity of biological barrier systems in the lunar receiving laboratory before it was put in service by NASA. This group also developed the internationally accepted biohazard warning symbol, which is as widely accepted in the field of biological research as the familiar radiation warning symbol is in the field of radiological research. For several years this same group of environmental specialists have been involved in contamination control research, development, and consultation for the National Cancer Institute laboratories.

## CLIENTS

**Who uses ECS and how successful has it been?** Over the years, ECS has performed services for more than 150 major industrial clients, many of whom are listed in the Fortune 500 list. Our customers include such well-known companies as General Electric, Xerox, Du Pont, and General Foods, to mention a few. After turning a profit in 1970, ECS finally is earning at a rate which lets us keep our head up with other Dow businesses. I think our performance would compare very fávorably with that of other environmental companies.

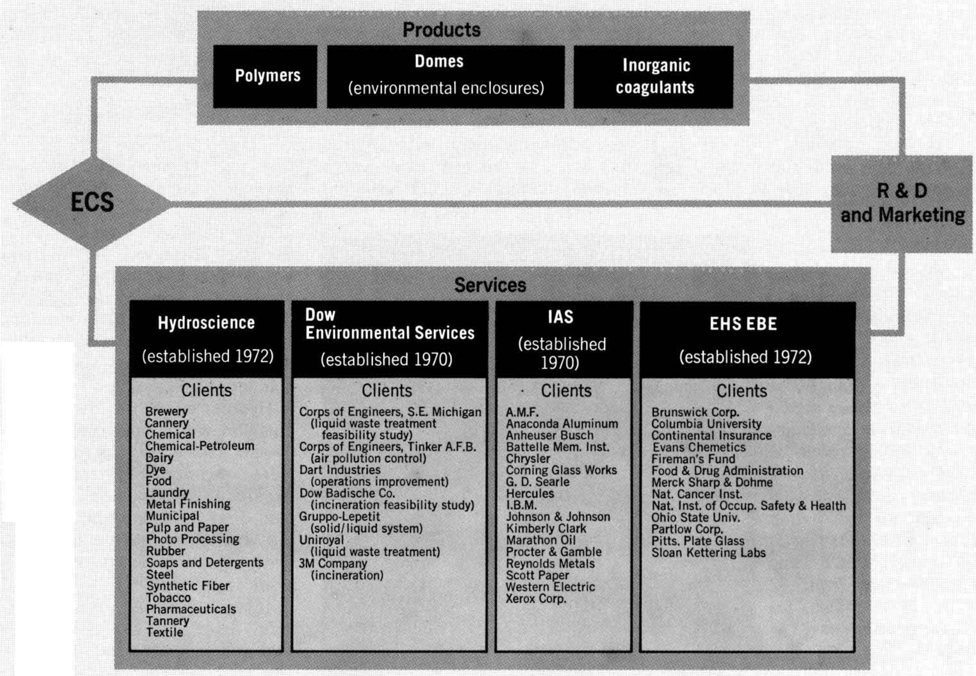
**Are there examples of environmental products or services in which Dow is no longer interested?** Earlier the company marketed Surfpac, a biological oxidation media made of polyvinyl chloride. At that time Dow was a producer of PVC; but the company no longer produces this material. In June 1973, the rights were sold to Envirotech, another environmental company. But Surfpac is the only environmental business activity that Dow's ECS has sold.

## SHOWCASE

**What examples can you cite of ECS activities?** Hydroscience was retained by the Great Lakes Basin Commission to evaluate the feasibility of developing water quality related models for the Great Lakes. The study involved a review of existing data and modeling techniques as well as the development of a specific modeling framework that could be applied for water quality management control of the lakes. A demonstration model, concentrating on a zone of Lake Erie, was prepared to demonstrate the practical use of certain modeling techniques. A continuing investigation developing a ranking of problems within the lakes and creating a framework for further analysis of the problem is under way.

A good example of our IAS work involved determining the cause of an intermittent odor in extruded plastic film. The problem was serious, since

## ECS at a glance



**Hydroscience**
(established 1972)
Clients
Brewery
Cannery
Chemical
Chemical-Petroleum
Dairy
Dye
Food
Laundry
Metal Finishing
Municipal
Pulp and Paper
Photo Processing
Rubber
Soaps and Detergents
Steel
Synthetic Fiber
Tobacco
Pharmaceuticals
Tannery
Textile

**Dow Environmental Services**
(established 1970)
Clients
Corps of Engineers, S.E. Michigan
  (liquid waste treatment feasibility study)
Corps of Engineers, Tinker A.F.B.
  (air pollution control)
Dart Industries
  (operations improvement)
Dow Badische Co.
  (incineration feasibility study)
Gruppo-Lepetit
  (solid/liquid system)
Uniroyal
  (liquid waste treatment)
3M Company
  (incineration)

**IAS**
(established 1970)
Clients
A.M.F.
Anaconda Aluminum
Anheuser Busch
Battelle Mem. Inst.
Chrysler
Corning Glass Works
G. D. Searle
Hercules
I.B.M.
Johnson & Johnson
Kimberly Clark
Marathon Oil
Procter & Gamble
Reynolds Metals
Scott Paper
Western Electric
Xerox Corp.

**EHS EBE**
(established 1972)
Clients
Brunswick Corp.
Columbia University
Continental Insurance
Evans Chemetics
Fireman's Fund
Food & Drug Administration
Merck Sharp & Dohme
Nat. Cancer Inst.
Nat. Inst. of Occup. Safety & Health
Ohio State Univ.
Partlow Corp.
Pitts. Plate Glass
Sloan Kettering Labs

the odor made the film unsuitable for use as a food wrap. Using gas chromatography–mass spectrometry, we were able to identify the odor-causing component. It was ultimately traced to the lubricant in a pump used in the extrusion process. Changing to a different lubricant solved the problem.

ECS designed a solid and liquid waste incineration facility at the 3M Co. (Minneapolis, Minn.). This facility is more than a $5 million industrial waste incinerator based on one that Dow built a number of years ago at its Midland, Mich., manufacturing location. In this specific example, ECS, working in close cooperation with 3M engineering, took the item from its conceptual phase, all the way through the engineering design of the operating unit and participated in start-up. So here is an example of Dow expertise being translated to another industrial waste disposal facility. We are currently designing similar disposal facilities for other industrial clients.

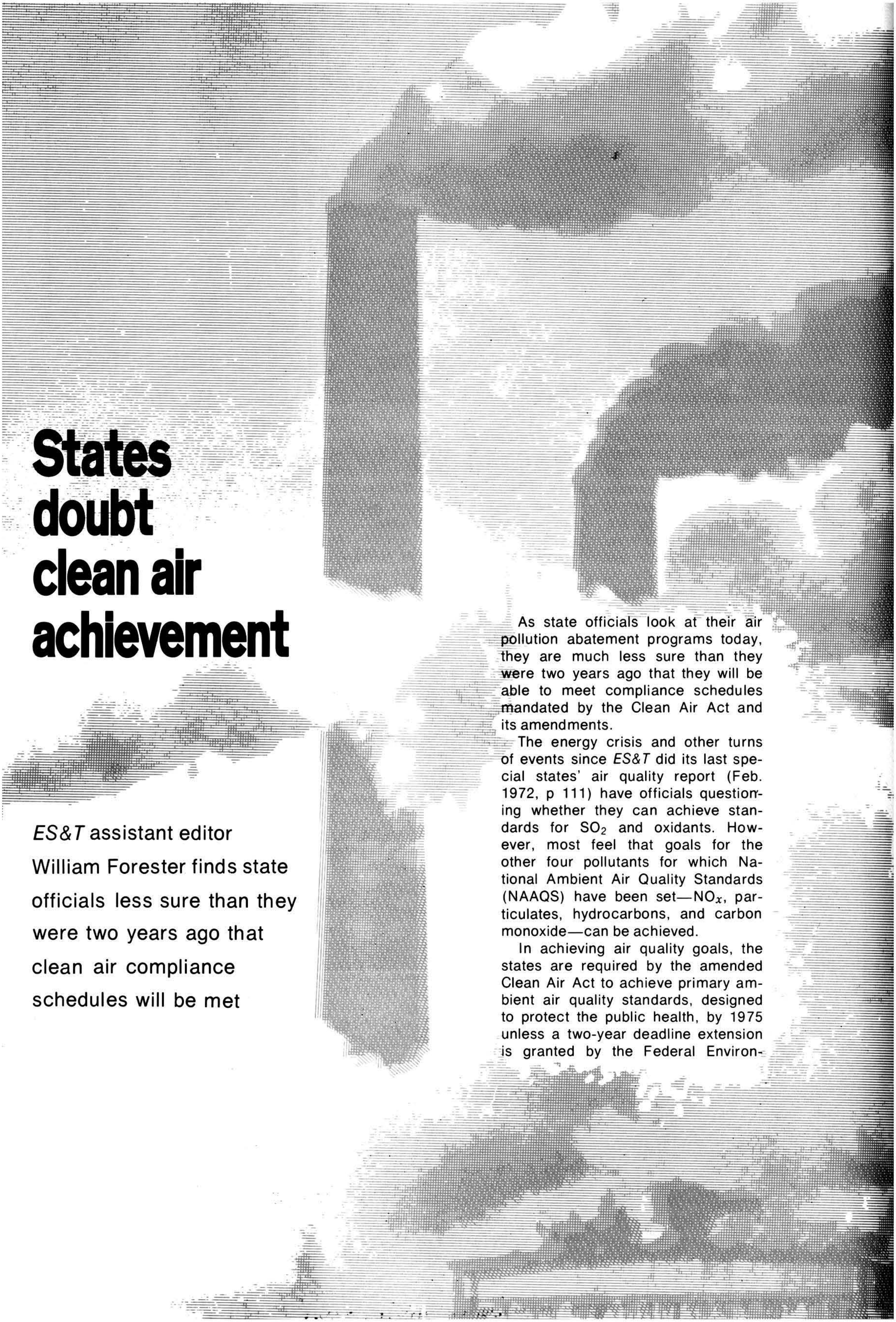
The National Association of Photographic Manufacturers has retained Hydroscience, Inc. to perform a detailed study of the pollutional characteristics of the 50 major chemicals involved in the industry. These studies included a definition of the biodegradability of the substrates, their relative toxicity, and their compatibility with municipal waste treatment. The study developed several innovative methods of examining the characteristics of industrial compounds. To widely disseminate the information, NAPM, in cooperation with Hydroscience, is now sponsoring three national symposia where information developed from the studies, as well as peripheral information, will be presented to the industry.

> ***"ECS is earning at a rate which lets us keep our head up with other Dow businesses."***
>
> ECS's McKennon

**Is ECS active outside the U.S.?** Hydroscience has done work in Canada, Europe, and Latin America, and our DES group has done a job for Gruppo Lepetit, an Italian pharmaceutical manufacturer in which Dow has a substantial interest. We have not set up any ECS-type organization outside the U.S., however, and plan to further develop our U.S. business before planning extensive work elsewhere.

## PERSONAL ASIDE

**What was your experience at Dow prior to the ECS assignment?** My background is heavily R&D oriented, but does include a stint in field sales management. For a number of years I was involved with Pusher chemicals—chemicals used to enhance the process by which oil is recovered from underground. (Pusher is part of another of Dow's 30 businesses—in this case, the mining and petroleum industry products business.) When Dow developed its ECS services, this business began plowing some new ground in terms of how a corporation like Dow can best perform this type of service-oriented work. We have to think in terms of earning a return for Dow on people and technology instead of railroad cars full of products. It's quite challenging and rewarding. As you have seen, ECS is now marketing a whole raft of new services, something that Dow has not done a whole lot of in the past.



# States doubt clean air achievement

*ES&T* assistant editor William Forester finds state officials less sure than they were two years ago that clean air compliance schedules will be met

As state officials look at their air pollution abatement programs today, they are much less sure than they were two years ago that they will be able to meet compliance schedules mandated by the Clean Air Act and its amendments.

The energy crisis and other turns of events since *ES&T* did its last special states' air quality report (Feb. 1972, p 111) have officials questioning whether they can achieve standards for $SO_2$ and oxidants. However, most feel that goals for the other four pollutants for which National Ambient Air Quality Standards (NAAQS) have been set—$NO_x$, particulates, hydrocarbons, and carbon monoxide—can be achieved.

In achieving air quality goals, the states are required by the amended Clean Air Act to achieve primary ambient air quality standards, designed to protect the public health, by 1975 unless a two-year deadline extension is granted by the Federal Environmental Protection Agency. The act also requires that secondary ambient air quality standards, designed to protect the public welfare, be achieved within a reasonable time.

Each state has been required to submit a plan for the implementation, maintenance, and enforcement of the NAAQS within each Air Quality Control Region (ACQR), or portion thereof, within its state boundaries. At this time, the major portions of these State Implementation Plans (SIP) have been approved by the EPA, which is responsible for surveillance of the plans, and are now being pursued.

Further, the data acquired by state air quality monitoring stations established under the plans must be submitted to the EPA on a quarterly basis. These data furnish the agency the basis both for periodic air quality information evaluation and for assessment of the rate at which SIP's are achieving their goals.

### Implementation plans

Most state officials feel that their original implementation plans generally have proved to be adequate, although some changes were made. These mostly resulted from $SO_2$ emission problems and the addition of transportation control strategies by the EPA. Specific transportation controls were not required originally.

In the New England states, **Connecticut** has requested two changes in its original plan. The first would eliminate the need for an already-granted extension for particulates because of a program to burn fuels. The other would revise the state's monitoring system to include 12 telemetered, complete stations. **Rhode Island** has tightened its restrictions on visible stack emissions by substituting Ringlemann 1 (clear stack emission) for Ringlemann 2 (light gray) standards.

Original EPA-approved implementation plans generally have been proved adequate for **New York State.** However, their Division of Air Resources Director Alexander Rihm, Jr., feels that a final judgment cannot be made until full implementation is complete and a reasonable time is allowed to assess the effects. Likewise, **New Jersey's** Bureau of Air Pollution Control chief, William A. Munroe, says the adequacy of that state's plan can be evaluated only when ultimate federal standards/achievement deadlines are firm.

**Delaware** has encountered a major problem with respect to flexibility in granting temporary relief from regulatory requirements, especially in the case of $SO_2$ regulations. A revision of their original plan is being prepared to deal with such situations. **Maryland** officials report that their plan for achieving secondary $SO_2$ standards had to be revised. However, the revision submitted was based on the annual average that subsequently has been rescinded by the EPA. Their implementation plan for achieving CO, HC, and oxidant standards required additional promulgation by EPA. Also, Maryland's implementation plans for transportation controls in both Baltimore and Washington, D.C., areas have been granted two-year extensions.

**Virginia** anticipated the same problem for transportation controls in the highly urban Washington, D.C., area. Officials requested, and were granted, two-year extensions for Northern Virginia. In another matter, the state received an 18-month extension for meeting secondary standards for particulate matter in its State Capital Region (Richmond). However, they later notified EPA that these standards would be met before June 1975, and that the extension would not be needed.

In **South Carolina,** W. G. Crosby, chief of South Carolina's Bureau of Air Quality Control, feels their $SO_2$ standards also were too strict. He especially is critical of original EPA guidelines that "failed to deal with maintenance and prevention of significant deterioration."

The **Georgia** plan generally has been proved adequate, officials claim. However, specific regulations dealing with emissions from cotton gins and fertilizer plants, as well as authority to require source monitoring and operating permits, have been added. The state also experienced problems because of a National Resources Defense Council (NRDC) suit against the EPA's approval of a regulation allowing the use of high emission stacks. The issue was resolved in favor of NRDC.

**Alabama** has adopted additional regulations for particulates from coke ovens, pulp mills, wood waste boilers, and primary aluminum plants. The state also has increased its allowable $SO_2$ emissions from fuel combustion. As with other states, this was undertaken because of the energy crisis—but also because of the development of better modeling capabilities.

A law suit also figured in **Kentucky's** attempt to set standards. A ruling in June of last year, Buckeye Power et al. vs. EPA, said EPA failed to allow for public comment. In **Tennessee,** initial $SO_2$ emission standards proved overly restrictive. These standards were revised.

**Ohio** also experienced problems with its regulation of $SO_2$ sources. The state's original method of compliance was to switch fuels from coal to distillate oil or gas. Officials have requested a two-year extension for achieving the air quality standard for oxides of sulfur, but the request has not been granted. Officials in **Indiana** complain that their original plan has proved to be inadequate in several areas. Problems were encountered with regulations, emergency episodes, source emission data, and local agency relations. **Arkansas** originally had to toughen its plan before the EPA would approve it.

### Other Midwest states

The principal implementation plan problem encountered in **Illinois** was in conducting the necessary level of surveillance and enforcement activity to bring some 19,000 industries into the program by mid-1975, according to John J. Roberts, manager of that state's Division of Air Pollution Control. Active changes in Illinois' plan have been minor, Roberts says. Generally, these resulted from an inadequate opportunity to review the economic impact of regulations in one or more segments of the state's industry, such as grain elevators.

**Wisconsin** has found original standards inadequate to deal with oxidants in rural areas, where this pollution is more common than in urban areas. Officials say the federal EPA oxidant strategy needs re-evaluation. A particular disappointment has been in the difficulty of reducing particulates, especially in urban areas, by as much as officials had predicted. **Minnesota** has added a regulation on asbestos. That state also has adopted a Transportation Control Section, after the EPA was forced in court to cancel time extensions on carbon monoxide compliance.

Two substantial amendments have been added to **Iowa's** plan during the past two years. One provides the Department of Environmental Quality with the authority to require self-monitoring by source owners, the other the authority to make available to the public emissions data by source name. Again, a principal criticism is that reinterpretation of the Clean Air Act by federal courts requires frequent and substantial changes.

**Nebraska's** original plan lacked sufficient legal authority to limit emissions in areas that were primarily agricultural. Present proposed regulations correct this problem. Nebraska requested an extension for $NO_2$ compliance, which was denied. The original plan for **Kansas** has been adequate with regard to the development of a workable plan to control point sources of pollution.

**Colorado,** however, plans to rewrite its plan totally sometime this year. The original plan is too rigid in concept and fails to take into consideration the high altitude effect on emissions, according to Gerald P. Wood, director of the Colorado Air Pollution Control Division.

### Planning in Southwest

**Texas** encountered implementation planning problems with transportation controls, indirect source controls and nondegradation. Other problems include imposed time limits and differences with the EPA regarding the most suitable approaches. The state requested two-year extensions for photochemical oxidants in two air quality control regions when their original plan was submitted. The extension was approved, but approval was revoked by the NRDC vs. EPA court ruling of January 1973. The *Federal Register* (Nov. 6, 1973) promulgated an EPA transportation control plan for Texas that extended attainment dates for Regions 7 and 9 for two years and Region 8 to June 30, 1976.

**New Mexico's** original plan was inadequate as to $SO_2$ emission regulations in its Four-Corners Power Plant area, according to NOAA modeling results in the Southwest Energy Study. The EPA assumed jurisdiction and promulgated federal standards. The major problems occurring for neighboring **Arizona** concerned jurisdiction. R. F. Iacobelli, administrative engineer for the state department of health, noted that the federal EPA had contacted operators directly instead of working through the state. This resulted in some confusion over disapproved $SO_2$ and particulate strategies. Also, Arizona was granted a two-year extension, to May 31, 1977, for attaining CO standards.

The state of **Washington** reports that its original plan generally has proved to be adequate. Major problems have occurred, however, in the development of transportation control plans and plans for complex sources. **Idaho's** plan indicated that the achievement of the NAAQS for particulates was doubtful because of high particulate loadings from fugitive sources. Officials say achievement of this standard is still in doubt. Idaho has been granted a two-year extension for achieving the primary $SO_2$ standard in the Northern Idaho/Eastern Washington interstate region.

### State standards

Some states set stricter standards than those required by the EPA. Reasons for this vary according to the types of industry in the particular states to the transportation situations, which in such cases as Los Angeles require special guidelines. For a look at what additional standards some of the states have set see Table 1.

### Regional standards?

The exclusion of regional standards from the Clean Air Law presents few problems for the states, except in cases where a state's air quality is affected seriously by neighboring pollution sources. **Connecticut** complains that its air is much affected by **New York** and **New Jersey** polluters, and that they are powerless to do enough about it. Such rural states as **Vermont** and **New Hampshire** feel their standards should be more stringent than the national standards. States that are more industrialized feel it would be impossible to keep their air as clean as the other states, and that they should not be forced to attempt such drastic measures. **New York,** for example, says that secondary particulate standards may be attained there, but not without severe economic and social dislocations.

George P. Ferreri, director of **Maryland's** Bureau of Air Quality Control, sees a need for better un-

TABLE 1

**Some states have stricter controls for**

| | |
|---|---|
| **Alabama** | Secondary standards adopted for May 31, 1975 |
| **Arizona** | $SO_2$ |
| **Arkansas** | Adopted shorter time periods |
| **Colorado** | Particulates, $SO_2$ |
| **Connecticut** | NO |
| **Delaware** | CO, HC, $H_2S$ |
| **Florida** | $SO_2$, particulates, CO |
| **Georgia** | $SO_2$, $NO_2$ |
| **Hawaii** | Particulates, $SO_2$, CO, HC, oxidants, $NO_2$ |
| **Idaho** | NO |
| **Illinois** | NO |
| **Indiana** | $SO_2$ |
| **Iowa** | NO |
| **Kansas** | NO |
| **Kentucky** | $SO_2$ (Louisville) |
| **Louisiana** | NO |
| **Maine** | $SO_2$, particulates |
| **Maryland** | $SO_2$, particulates |
| **Minnesota** | $SO_2$, CO |
| **Mississippi** | NO |
| **Nebraska** | NO |
| **New Hampshire** | Adopted secondary standards as primary standards |
| **New Jersey** | NO |
| **New Mexico** | Immediately adopted secondary standards |
| **New York** | Particulates, fluorides, beryllums & $H_2S$ |
| **Ohio** | Secondary standards by July 1975 |
| **Puerto Rico** | NO |
| **Rhode Island** | NO |
| **South Carolina** | Fluorides |
| **Tennessee** | Ambient standards for COH & HF |
| **Texas** | CO, nonmentho & HC, photochemical oxides to particulate matter, $SO_2$, $H_2SO_4$, HS |
| **Virginia** | Adopted secondary standards in Northern Virginia, fluorides, beryllums |
| **Washington** | $SO_2$ |
| **Wisconsin** | NO |

TABLE 2

Extent of states monitoring networks varies

| | Stationary | Mobile | Continuous | Periodically scheduled |
|---|---|---|---|---|
| Alabama | 84 | 6 (moveable) | 12 | 72 |
| Arizona | 33 | 1 | 10 | 24 |
| Arkansas | 46 | 0 | 0 | 46 |
| Colorado | 108 | — | 15 | 87 |
| Connecticut | 100 | 0 (12 planned) | 40 | 60 |
| Delaware | 17 | — | — | — |
| Florida | — | — | — | — |
| Georgia | 120 | 1 | 35 | 86 |
| Hawaii | 21 (planned) | 0 | 3 | 18 |
| Idaho | 22 | 0 | 2 (planned) | 20 |
| Illinois | 151 | 5 | 32 | 144 |
| Indiana | 19 | 0 | — | — |
| Iowa | 100 | 11 | 23 | 77 |
| Kansas | 55 | 5 | 55 | 5 |
| Kentucky | 107 (20 more planned) | 0 | 8 | 99 |
| Louisiana | 53 | 0 | 8 | 25 |
| Maine | 19 | 2 | 5 | 19 |
| Maryland | 39 | 0 | 8 (3 more planned) | 31 |
| Minnesota | 122 | 0 | 26 | 96 |
| Mississippi | 29 | 1 | 4 | 25 |
| Nebraska | 55 | 0 | 5 | 50 |
| New Hampshire | 35 | 3 (1 planned) | 3 | 32 |
| New Jersey | 78 | 4 | 18 | 60 |
| New Mexico | 71 | 2 | 7 | 66 |
| New York | 305 | 6 | 35 (15 planned) | 280 (20 planned) |
| Ohio | 278 | 0 | 61 | 217 |
| Puerto Rico | 23 (under construction) | — | — | — |
| Rhode Island | 23 | 0 | 3 | 20 |
| South Carolina | 95 | 0 | 25 | 70 |
| Tennessee | 52 | 7 | 13 | 46 |
| Texas | 140 | 2 (3 planned) | 17 | 118 (162 planned) |
| Vermont | 4 | — | 4 | — |
| Virginia | 102 | 0 | 10 | 146 |
| Washington | 50 | 0 | 25 | 25 |
| Wisconsin | 158 | 2 | 7 | 151 |

derstanding the "synergistic effect" of combined pollutants, which can differ strikingly from region to region. Ferreri says that although there is not enough information to support different standards for different regions at this time, it is known that temperature and humidity, which differ from region to region, do influence the effect of the pollutants. He points out that vegetation may be more susceptible in areas where $SO_2$ and oxidants together are a problem. All this needs to be taken into account in setting standards, he says.

The executive director of **Virginia's** State Air Pollution Control Board, William R. Meyer, likewise sees a definite need for clearer recognition of background factors, especially with oxidants and particulates in special areas. But, pending completion of a National Academy of Sciences study of the standards, he sees no need for a change in standards as such. **Florida** officials point out that within an AQCR, unlike emission standards have presented problems there when sources are separated only by a state boundary. They feel that their present air quality standards are satisfactory.

James W. Cooper, director of **Alabama's** division of Air Pollution Control, tells *ES&T* that for the regional divisions to be effective, a significant amount of responsibility should be delegated to the regional office. As it stands presently, he says, the primary effect of regionalization has been only to create an additional stage of review. **Kentucky** feels that policy throughout the various EPA regions is not consistent, and that the regions require extremely burdensome reporting requirements.

### Homogeneity needed

Harry D. Williams, director of **Indiana's** Air Pollution Control Division, says the AQCRs, as presently set up, do present problems because some are rather large and not homogeneous in terms of their air pollution problems. In **Kansas,** Howard F. Saiger, chief of the Air Quality and Occupational Health Section, says that the standards should be revised for his area to recognize the existence of high uncontrollable background conditions. High winds and low rainfall there cause special particulate problems that are not adequately faced by the present standard setup, he said.

James Lefler, Air Pollution Control Division engineer for **Nebraska,** says the AQCR designations in his state are a "farce." Adjacent counties with similar air quality problems were not included in the same region. In other cases, counties included in the same region show no similarity in air quality or industrial sources, he said. **Arizona** officials feel that air quality standards should vary by regions. Iacobelli points out that fugitive dust in the entire southwest desert area is difficult to control and that particulate standards should be less stringent because of this.

### Monitoring

Monitoring networks in the various states have been expanded enormously during the past two years. Most of the states undertook special modeling or testing of implementation plans before deciding specifically on the final form of their plans.

TABLE 3

### Officials view achievement of Federal standards

| | Primary | Secondary | 2-Year ext. granted |
|---|---|---|---|
| Alabama | WBA | WBA | Yes |
| Arizona | Yes | d | Yes |
| Arkansas | p.e. | p.e. | No |
| Colorado | d | d | Yes |
| Connecticut | d | d | Yes |
| Delaware | WBA | p.e. | No |
| Florida | WBA | d | Yes |
| Georgia | WBA | WBA | No |
| Hawaii | WBA | WBA | No |
| Idaho | WBA | WBA | Yes |
| Illinois | d | N.A. | No |
| Indiana | WBA | d | Yes (over-rated in count) |
| Iowa | WBA | WBA | No |
| Kansas | d | d | No |
| Kentucky | p.e. | p.e. | Yes |
| Louisiana | WBA | WBA | No |
| Maine | WBA | WBA | No |
| Maryland | p.e. | p.e. | Yes |
| Minnesota | WBA | WBA | Yes |
| Mississippi | WBA | WBA | No |
| Nebraska | WBA | WBA | No (request made) |
| New Hampshire | WBA | WBA | No |
| New Jersey | d | d | Yes |
| New Mexico | d | d | No |
| New York | d | d | Yes |
| Ohio | WBA | WBA | No (request made) |
| Puerto Rico | WBA | WBA | No |
| Rhode Island | p.e. | WBA | No |
| South Carolina | d (Charleston) | d (Charleston) | No |
| Tennessee | p.e. | p.e. | No |
| Texas | d | p.e. | No |
| Vermont | WBA | WBA | No |
| Washington | p.e. | p.e. | No |
| Wisconsin | p.e. | p.e. | No |

WBA = will be achieved; p.e. = problems exist; d = doubtful.

Virtually every state took advantage of federal funds for these projects.

In the **New Jersey–New York–Connecticut** Air Quality Control Region, the EPA IPP diffusion model was used to evaluate particulates, as it was in other regions. But modeling is still being employed in New Jersey, where the state is preparing a plan for indirect sources. Munroe points out that the so-called ERT diffusion model has been made workable for point and area sources. He anticipates that, where applicable, this model will be used for impact statement evaluations and for preparation of any forthcoming plans to achieve air quality standards.

**Delaware** officials point out that plans there also were tested by the EPA IPP model, as were the **New Jersey** and **Pennsylvania** plans. The results lend more confidence to the adequacy of Delaware's plans, they claim.

**Louisiana** utilized modeling, but the testing did not prove useful. Officials say the results were so inconsistent as to be useless. In **Alabama,** a rollback technique was used to indicate the adequacy of their original plan, due to what they saw as restrictive time limitations. However, subsequent plan revisions have incorporated diffusion modeling to assure the standards would be achieved. **South Carolina** had emission standards and experience prior to the 1970 amendments. Bureau of Air Quality Control chief, W. G. Crosby, noted that the state's particulate and $SO_2$ ambient standards, adopted five years before the national standards, are virtually the same.

Extensive modeling studies were conducted for major metropolitan areas in **Illinois** to evaluate the cost and effectiveness of alternate control strategies. There, state officials have had continuing modeling and testing programs since 1972. Results from these studies are the basis for Illinois' current re-evaluation of $SO_2$ regulations. In **Ohio,** special modeling (Air Quality Dispersion Model) was done in the "worst case" example regions. In **Arkansas,** an AQDM model was used to test regulations only in the most heavily concentrated area (Little Rock) on the assumption that if they were adequate there, they would be satisfactory for the remainder of the state.

The pattern set by **Arkansas** was the one followed in most of the western states, modeling and testing were used only in the most heavily populated regions. Exceptions are the two coastal states of **Washington** and **Oregon** where conditions forced a more comprehensive set of modeling procedures. Washington, for example, used modeling for parts of the Puget Sound Region, and the rollback technique for most of the rest of the state.

The extent of the monitoring network in the various states is demonstrated in Table 2. The chart shows wide differences in units set up to gather data. It also reflects the differences in monitoring needs of the various states.

### Enforcing the laws

In almost every case, state officials feel their enforcement laws have been adequate to handle major violators. The only two exceptions are **Illinois** and **Tennessee,** of 38 respondents to an *ES&T* questionnaire. Illinois reports that although enforcement programs both at the state and local levels have been aggressive, the magnitude of the problem is too great. They say this is true especially when the number of sources with mid-1975 deadlines are considered. They hope that future coordinated efforts by state and federal agencies will prove effective in the cases of major steel mill and electric utilities operations.

In **Connecticut,** the EPA has issued compliance notices to two companies. There have been 850 notices of violation, with 254 orders issued since Oct. 1, 1971. The maximum fine in Connecticut is $5000 per week. The most significant action to date has been a $2500 fine and a required $400,000 performance bond for a firm that was delinquent in compliance. In another possible enforcement compliance problem, Connecticut feels that the standard for photochemical oxidants will not be met in several areas of the state. Transportation controls are being required for other areas. However, dates for achievement of these goals have not yet been decided.

**Rhode Island's** laws provide a jail sentence, as well as $500-per-day fine. In all, that state undertook 20 enforcement actions during 1973. As with most other states, Rhode Island feels there will be no problem meeting primary air quality standards, but that energy considerations will delay their goal for meeting secondary standards. For a full look at the states' expectancy in meeting primary and secondary goals, along with those states granted two-year extensions, see Table 3.

In the past, delays have been encountered in **New York** due to lack of legal personnel, but officials say this has been remedied. The enforcement situation also has been cleared somewhat by a recent compromise ruling in a NRDC case where the federal EPA was called into question for approving New York implementation plans while being aware that state law provided for variances on the basis of economic cost. Officials feel enforcement action has proceeded well, with almost 200 commissioner's orders issued during the past two years.

In lieu of levying fines against violators, as provided by law, **New York** has more often required source owners to post performance bonds to ensure the completion of state-ordered compliance schedules. New York's most significant action to date is a current lawsuit against coke oven operators in the western part of the state. It will be some time, however, before the outcome of this case will be known, officials feel.

**New Jersey** currently is invoking about 120 enforcement actions each month. Penalties have ranged from $100 to $250,000, and a penalty of up to $2500 per day is authorized for each continuing violation. New Jersey is one of several states that has solid data on results from its permit and certificate programs. They claim the potential emissions inventory for solid particles during 1973 was reduced by 52,563 tons/year and solvents, acids, and chemicals by 5005 tons/year.

**Delaware,** prior to July 1973 changes in the state law, felt it was burdened with excessive compulsory conciliatory efforts, inadequate penalties, and cumbersome enforcement procedures. The EPA had stepped in to enforce compliance in at least two major cases because of the state's inaction.

Officials in **Virginia** likewise feel their state law now is adequate, after some clarifications suggested by the State Air Pollution Control Board were written into the law by the legislature. The one exception, according to Paul E. Wilkins, chairman of the State Air Pollution Control Board, is a provision interpreted to mean that the state has no authority to regulate leaf burning where a local government has its own ordinance. This is thought to be true even in cases where local ordinances are less stringent than state regulations.

**Georgia** feels that the most significant aspect of its enforcement program is that the state has been able to effect the necessary controls in almost all cases on a relatively cooperative basis. **Tennessee's** most significant action has been a suit for compliance against the Tennessee Valley Authority.

Open burning laws have been the hardest to enforce for **Arkansas. Indiana** officials feel satisfied with their laws. In the cases where the EPA has stepped in to enforce regulations, Indiana officials claim it was not because the state was unable to act but "because of the EPA's highly legalistic interpretation of what is required by the Clean Air Act, and their concern primarily with form versus substance of compliance programs." The state's primary problem has been to determine compliance from sources whose emission is not from a stack.

### More Midwest activity

Less-populated **Kansas** has been highly active in its enforcement programs. More than 5000 firms have been evaluated for compliance with regulations during a three-year period. Such evaluations include reporting, on-site inspections, emission calculations, and follow-up or required corrective action. More than 400 enforcement orders have been issued, two of which required court action. **Nebraska** presently has 24 sources on compliance schedules, and one operation has been closed down by injunction.

While **Iowa** has held 12 enforcement hearings during 1973, its most significant action was the closing of a cement plant according to emergency order procedures. **Minnesota** claims in most cases it has been able to get compliance programs under way without legal action. Although the EPA stepped in and issued compliance orders in three cases, state officials point out that compliance negotiations by the Minnesota Pollution Control Agency already were under way with the companies in question.

**Minnesota** presently has instigated legal action in two cases, one against Reserve Mining for dumping taconite tailings in Lake Superior, and another against the Fry Roofing Co. **Wisconsin** is critical of the EPA for stepping in where the state had already acted. They point out that the state has not asked the agency to intervene, nor do they feel they have sources they are unable to control.

**Texas,** since November 1967, has filed 178 court cases and has invoked 84 board orders. The highest penalty collected was from Armco Steel for $250,000. The Texas penalty provision is $50 to $1000 for each day of violation. Industry in **New Mexico** has kept legal proceedings to a bare minimum. So far, one wood waste burner was taken to court and forced to install pollution controls.

**Arizona** has found the abatement order—it issued four during 1973—to be the most effective enforcement device available at the state level. The most significant action so far for the state of **Washington** has been the several variance hearings to adopt a control program for the huge copper smelter at Tacoma. **Idaho** has found civil penalty procedures to be too cumbersome, and to date has undertaken criminal action in all cases where court action has proved necessary. **Hawaii** has found its laws to be adequate.

### Industry makes progress

Although tremendous progress has been made by many states in their programs to abate industrial pollution, some nagging problems with sulfur fuels and hydrocarbons persist. As to the major offenders, this tends to vary according to the kinds of industries prevalent in the individual states.

**Connecticut** is especially concerned with the problems arising from hydrocarbon emissions and the burning of $SO_2$-containing fuels. **Rhode Island** industries have made progress in dealing with the pollution from gray iron foundaries and incinerators, but is still faced with problems from other foundries, textiles, and animal rendering plants. A special regional problem exists in New England because of pollution from wood burners used in wood industries. In numerous cases, wood is burned in waste heat boilers where plant size is small and abatement costs comparatively large.

In **New York,** most industries are complying with industrial emission standards, although problems do exist with iron, steel, and graphitizing process industries in the Niagara area. **New Jersey** has made particular progress in reducing $SO_2$ and particulate emissions. Officials are seeking to achieve reductions also in HC and $NO_x$ as alleged precursors to photochemical oxidants.

Considerable progress has been made in **Delaware** in controlling $SO_2$ and particulates. However, problems are being experienced with electric arc steel furnaces emitting particulates.

The most severe problem in **Maryland** is controlling emissions from existing coke ovens. A flue gas desulfurization pilot system program has been set up to combat this problem, but an evaluation has not yet been completed. Galvanizing and glass manufacturing industries are other major problems.

A particular worry in **Virginia** is with small foundries, which cannot afford the high cost of control equipment adequate to meet emission standards. $SO_2$ emissions from coal-burning plants is the biggest problem in **South Carolina.** Particulate sources there are being controlled very well, according to Chief Crosby. **Florida** likewise is faced with problems in sulfur recovery and particulate control areas.

### Confronting deadlines

Robert A. Collom, Jr., **Georgia's** Air Quality Control Section chief, predicts that all industries in his state will meet 1975 compliance schedules. The larger industries are all following acceptable schedules, although some smaller industries are slightly behind at this time. The NRDC court challenge to $SO_2$ and particulate regulations has caused some uncertainty among state industry personnel as to what they can and should do, according to Collom.

A major problem in **Alabama,** says James W. Cooper, director of that state's Division of Air Pollution Control, is with slow equipment delivery. He cites steel shortages and demand increases due to 1975 compliance deadlines as reasons for delays. **Mississippi** is experiencing problems both with $SO_2$ control from large coal-fired boilers and $H_2S$ problems from sour crude gas processing.

Incinerators in various municipalities are the biggest headache in **Louisiana.** Officials say industry as a whole tends to cooperate, while municipalities tend to drag their feet. Delayed deliveries of control equipment is a problem in **Tennessee** where compliance schedules have been affected and difficulty in meeting 1975 compliance mandates is expected. **Kentucky's** director of the Division of Air Pollution, John T. Smither, says excellent progress has been made in reducing particulates. However, $SO_2$ control at TVA power plants, and at coke plants, as well as TRS control at pulp mills remains a problem.

The two major segments of industry in **Illinois** creating special problems are electric utilities and steel manufacturers. Progress has been made in the control of steel mill operations but full control probably will not be achieved until 1976, officials believe. Court proceedings and proposed federal legislation will determine the state's control over the electric utilities. **Indiana** has encountered problems from coke ovens, steel manufacturing, and power plants. For **Ohio,** electric utilities and coke ovens present major problems.

### Problems differ

In Colorado, oil shale extraction is already becoming a pollution problem. If plans for full development are realized, this industry could create problems of great magnitude. Industry in **Kansas** has encountered problems in the areas of glass fiber manufacturing, ammonium nitrate manufacturing, and alfalfa dehydrating. Obtaining equipment has likewise caused compliance apprehension for officials in Kansas. **Iowa** has experienced problems with fugitive dust regulations, particularly for the grain-handling industry, $SO_2$ regulations for coal-fired power plants and control equipment breakdowns in the cement industry.

**Minnesota** officials especially voice concern over the Federal Energy Board ban on coal-to-oil conversions for utility plants. This will affect compliance, they claim. In addition, refineries, fertilizer plants, and small sulfuric acid and nitric acid plants are problems, but officials except to resolve them. **Wisconsin's** Air Pollution Control Section chief, Douglas W. Evans, feels progress there generally has been good. Exceptions, however, exist for coke manufacturing, pulpmills, some foundries, and municipal incinerators, which Evans calls the worst offenders.

Charles R. Barden, executive director of the **Texas** Air Control Board, says his state is making progress in all areas with the exceptions of smelting sources, plywood veneer drying, and automobile emissions. Robert A. Harley, assistant chief of **New Mexico's** Air Quality Division, reports with optimism on two important air quality developments in his state. One is that New Mexico has issued a construction permit for the nation's first flash smelter (Phelps-Dodge), which will achieve 90+% control of $SO_2$. The second is that the New Mexico Public Service Co. has designed and will build a 300+-MW coal-fired power plant that will achieve 90% $SO_2$ control.

Material deliveries and technical

TABLE 4

**States' budgets, personnel both increase**

| | Budget | Personnel today | 2-Year change in personnel |
|---|---|---|---|
| **Alabama•** | $1.2 million | 45 | +36 |
| **Arizona** | 2.2 million | | 100% increase |
| **Arkansas** | 451,233 | | Increase |
| **Colorado** | 1.2 million | 54 | +24 |
| **Delaware** | 500,000 | | Increase |
| **Florida** | 1.1 million | | Increase |
| **Georgia** | 1.1 million | 70 | +13 |
| **Hawaii** | 443,141 | 24 | +10 |
| **Idaho** | 363,400 | — | +6 |
| **Illinois** | 2.9 million | | $100 increase |
| **Indiana** | — | 50 | +36 |
| **Iowa** | 965,127 | | Increase |
| **Kansas** | 770,000 | 19 | +16 |
| **Kentucky** | 1.2 million | 85 | +43 |
| **Louisiana** | inadequate | | Same |
| **Maine** | 395,254 | | +9 |
| **Maryland** | 2.2 million | | Increase |
| **Minnesota** | | | 10% increase |
| **Mississippi** | 590,000 | | +100% increase |
| **Nebraska** | 145,000 | 8 | +2 |
| **New Hampshire** | adequate | 20 (surveillance only | Increase |
| **New Jersey** | 2.3 million | | Increase |
| **New Mexico** | 350,000 | | +5 |
| **New York** | 12 million+ | | 10% increase |
| **Ohio** | 5.8 million | 175 | +159 |
| **Puerto Rico** | adequate | | Increase |
| **Rhode Island** | 275,000 | 17 | +5 |
| **South Carolina** | 950,000 | | Slight increase |
| **Tennessee** | 1.2 million | 83 | +27 |
| **Texas** | 6.4 million | 357 + $2.8 | +122 |
| **Vermont** | 250,000 | 15 | +14 |
| **Virginia** | 1.7 million | 108 | +60 |
| **Washington** | 2 million+ | | Small increase |
| **Wisconsin** | 454,000 (to be matched by EPA) | 49 | +20 |

problems are causing delays for **Arizona.** Likewise, copper smelters are currently falling behind schedule in meeting standards in the state. **Washington** is hopeful that 1975 goals will be met for all of its industry. **Idaho** has a serious problem with a smelter in the northern part of the state, even though it currently is controlling 80% of its $SO_2$ emissions. Topography and meteorology factors create $SO_2$ levels far above the standards. **Hawaii's** sugar cane industry has made progress in adding control devices. Cement plants and storage tanks, however, are still pollution problems there.

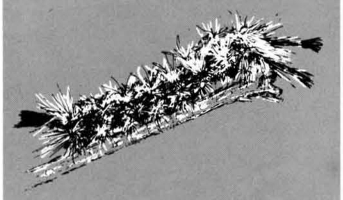
### Budgets, personnel, R&D

As budgets for the various states mostly reflect the salaries paid state personnel, the magnitude of the two tend to coincide. In general, the size of a state's total budget, generally reflecting the amount of industry in that state, also tends to reflect the size of its pollution abatement program. A comparison of both budgets and personnel is provided in Table 4. Also shown is the extent of personnel changes during the past two years, where such material is available.

Research and development at the state level is almost nonexistent. One notable exception is **California,** which funded an R&D program of $8.623 million from September 1970 to September 1973. More than 90% of this came from the California Transportation Fund and was designated for research related to motor vehicle air pollution. An additional $113,000 was provided by the state department of transportation. The balance of the money was appropriated from the California Environmental Protection Program Fund (CEPPF). Of the CEPPF money, $375,000 was designated for stationary source air pollution problems and for maintaining a repository of air pollution research reports. An additional $85,000 from the CEPPF was provided to investigate alternatives to open burning of agricultural wastes. Eight other states reported research and development programs, most of them very small in size.

On a happy note, almost every state that responded to the *ES&T* questionnaire reported that morale was high in their respective departments. Some uneasiness was expressed because of cramped office and working quarters due to rapid expansions in personnel, EPA's "excessive" paperwork, and possible program cutbacks due to the energy crisis. However, most workers are said to feel they already have made an impact on air pollution and will continue to do so as the decade continues.

## OUTLOOK



# The plight of the tussock moth

The search is on for DDT alternatives which not only can kill but can reduce the moth population sufficiently to prevent further damage

On January 3, 1974, the U.S. Forest Service requested an exemption from the DDT ban to control this summer's expected outbreaks of the Douglas-fir tussock moth in Oregon, Idaho, and Washington. The contingent use of DDT would be applicable to federal, state, and private lands in the three states. On February 26, 1974, Russell Train, administrator of the Environmental Protection Agency, granted the emergency exemption from the prohibitions of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), as amended.

### Conditions

Train made clear that the Forest Service must prove in May and early June that the extent of moth infestation has reached levels beyond the control of the moth's natural enemies. The entomological evaluation will be based on new egg mass counts which began last fall. A new egg mass density of $\frac{1}{10}$ egg mass (or larval population of 20 insects) per 1000 in.$^2$ of foliage will indicate the level at which the signficant foliage injury will occur. Factors affecting survival rate of larvae will be taken into account—winter stress, egg parasites, and virus infection.

Depending on weather conditions, spraying could start as early as June 1 and should end around July 15. At that time, DDT could be applied aerially to as many as 650,000 acres in order to destroy the moth larvae emerging from the dormant egg masses. This spraying would translate into approximately 49,000 lb of DDT, applied at a rate of 0.75 lb per acre.

Areas sustaining negligible or light defoliation will be excluded from spraying if virus infection level equals or exceeds 30%; for moderately or heavily defoliated areas, the virus infection level will have to exceed 50% for exclusion.

If and when the spraying begins, Train stressed that several restrictions will have to be observed:

- maintaining an unsprayed buffer strip of at least 200 ft along live streams and waterways
- marking of waterways on maps and photo aids for pilots, and of actual water areas with flags for prevention of accidental spraying of water
- stopping the spraying when winds exceed 6 mph or where temperature inversions exist
- removing of livestock and other domestic animals from the treatment areas
- placing of warning in public places within all areas to be sprayed, giving the date, time, and duration of the spraying
- licensing and proper training of applicators
- monitoring of actual spraying, using sensitized cards
- logging of all spraying for presentation to the EPA and public within 10 days following the conclusion of the project.

### History of outbreaks

The Douglas-fir tussock moth (*Orgyia pseudotsugata,* McDunnough) periodically defoliates Douglas-fir true firs, and other host trees in forests of the western U.S. Their earliest recorded outbreaks occurred in northeastern Washington in 1928–30, followed by others in northern Idaho and eastern Washington in 1950–55, and northern Idaho and western Montana in 1961–65. The current outbreak in northern Idaho, northeastern Washington, and eastern Oregon began in 1971.

During 1972, as many as 196,000 acres in Oregon and Washington were defoliated. The summer of 1973 witnessed the trebling of the moth epidemic, this time encompassing areas in Idaho and Montana. A total of 820,000 acres were damaged in the four states.

These outbreaks usually last two to four years in forested areas, beginning with a buildup phase the first year, an outbreak phase the next, and a declining phase the last (contributed by parasites and a natural polyhedrosis virus). They are best understood as direct functions of the moth's life cycle.

The life cycle of the moth begins in mid-May or early June when caterpillars $\frac{1}{8}$ in. in length emerge from egg clusters deposited the previous fall. With long hairs, the larvae can be dispersed by wind for long distances, and feast until late July or early August. At this time the larvae will have reached a full size of $1\frac{1}{4}$ in. when they enter their pupal stage. Wrapped in cocoons, they manifest themselves in 10–18 days as moths. Immediately, the female mates with the male, creating clusters of 250 eggs which are deposited and attached to or near the cocoons. These eggs represent the potential for defoliation the next year. The adults die before eating, soon after mating.

Since all the guilt of leaf eating is borne by the larvae, it is essential, to contain an infestation, that control measures be enacted as soon after

egg hatching as possible. For a single defoliation is usually all it takes to kill an evergreen tree. A partial defoliation stunts growth and weakens the tree to further attacks of insects and diseases.

**Outbreak consequences**

Timber loss during the last two summers has amounted to approximately 800 million board feet, roughly equivalent to 62,000 three-bedroom houses. Forest management estimates that it would cost some $25 million for reforestation by public and private landowners over a 20-year period.

These same losses are aesthetically unappetizing, equally to man and animals who seek natural covers. They encourage forest fires as more trees die and the inflammable debris builds up. Infestations also present a health hazard. To loggers and crew responsible for salvaging the killed wood, the hairs of the moths bring forth allergic reactions, such as welts, eczema, rashes, and breathing difficulties.

**Alternative control methods**

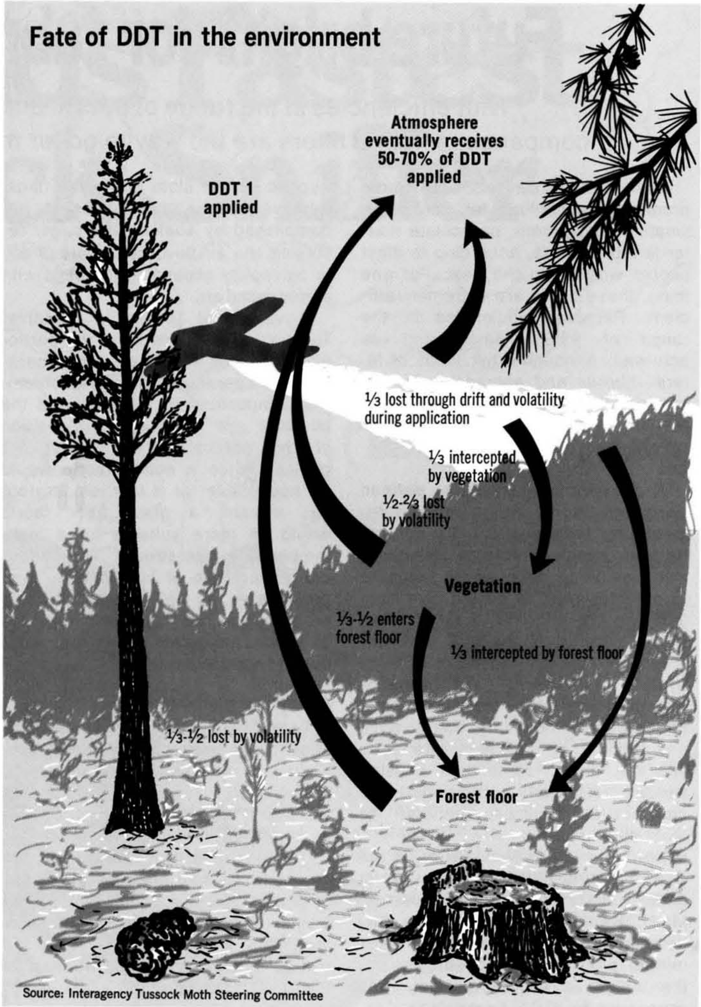
In the past, DDT has been proved very effective if applied within three days after 60% of the egg masses have begun to hatch. But the possibility of food chain contamination and much public controversy had canceled its use.

Field testing of other chemicals has produced considerable kills but none reduced the population sufficiently to prevent severe defoliation and tree mortality. Zectran, stabilized pyrethrins, carbaryl, trichlorfon, bioethanomethrin, Resmethrin, Phoxin, and Dursban are among the promising candidates which will be further evaluated. Malathion, Gardona, Imidan, and Methoxychlor showed low activity against the insect and will not be considered for future use.

Last year's field applications of the naturally occurring virus (nuclear polyhedrosis) or a bacterium (*Bacillus thuringiensis*), alone or in combination, have shown good controls of the tussock moth. But these biological agents are not registered, and EPA has not yet established protocols for safety testing. In addition, the aspect of mass producing—formulating, mixing, and handling—these materials has to be resolved before they can be put to operational use.

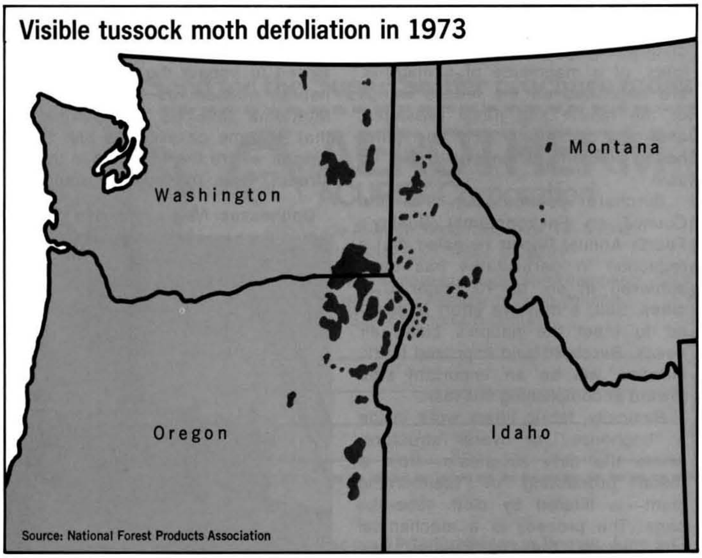
What is going to check future tussock moth epidemics? Will it be chemicals or microbials? For this summer, it will have to be DDT. Meanwhile, the development of reliable, registerable substitutes continues as top priority at the U.S. Forest Service. LCG

**Fate of DDT in the environment**



Source: Interagency Tussock Moth Steering Committee

**Visible tussock moth defoliation in 1973**



Source: National Forest Products Association

# Future bright for fabric filters

## With efficiencies in the range of 99.9% and favorable cost comparisons, fabric filters are the way to go for many source operators

With certain caveats, the most promising technology for controlling small, or submicron, particulate matter is fabric filters, according to most people working in the field. For one thing, these filters are extremely efficient. Removal efficiencies in the range of 99.9% easily can be achieved. Although other kinds of filters—fibrous and aggregate, for example—also are used successfully, results indicate they are effective only under specialized circumstances.

A fine particle usually is defined according to the range most detrimental for breathing, 0.1–1.0 micron. Related health problems, however, also can arise because of exposure to particles ranging all the way from 0.001 to 10 microns. John K. Burchard, director of the U.S. Environmental Protection Agency's Control System Laboratory at Research Triange Park, N.C., points out that fine particles not only cause haze and smog, but can penetrate deep into the lungs, sometimes causing serious respiratory conditions, and can act as transport elements for other pollutants.

Burchard told a Symposium on the Use of Fabric Filters for the Control of Submicron Particulates in Boston, Mass., recently that 50% of the particulates of the magnitude 0.01–0.1 micron will remain once they reach the lungs. (The symposium was sponsored by GCA Technology, Inc. and drew about 200 attendees.) Silicosis, bronchitis, and other lung conditions can result. Larger particulates, of a magnitude of 5 microns, are deposited on the mucus linings of the mouth and nasal passages, and can cause stomach and other health problems when swallowed, he said.

Burchard pointed out that the Council on Environmental Quality's Fourth Annual Report revealed that a reduction in particulates has been achieved in six of 10 major U.S. cities. Still, a massive effort is needed to meet the nation's clean air needs. Burchard said improved fabric filtration will be an important step toward accomplishing this task.

Basically, fabric filters work inside a "baghouse," or overall structure, where the dirty air steam—from a metal processing or fuel-burning plant—is filtered by cloth tube-like bags. The process is a mechanical one where the particulates are trapped on the cloth inside the bags. Removal of the particulates is accomplished by shaking the bags, reversing the air flow, quick jets of air, or by rapidly expanding the bags with compressed air.

A variety of fabrics is available. The choice depends upon the particular needs of the air-cleaning operation. Temperature, moisture, chemical composition of the gas, and the physical and chemical composition of the particulates all affect the choice. While a cotton fabric would be acceptable for a low-temperature gas stream, a glass fiber fabric would be more suitable for a high-temperature gas stream. The chemical composition of both the gas and particulates, as well as such physical properties as weight, affect the rates at which the fabric filters will wear out and need to be replaced.

### Alternative methods

Fabric filters compared well with such other particulate control techniques as scrubbers or electrostatic precipitators, according to John D. McKenna, vice president of Enviro-Systems & Research, Inc., Roanoke, Va. In a comparison with the Venturi scrubber, he said although the initial, or capital, cost for the fabric filter would be slightly higher, the operating costs would be less. Thus, the overall annual cost would be less for the fabric filter, he said.

In most cases, the scrubbing system—where the gas stream travels through a narrowed "throat" portion of an air duct into which water is forced to impact the particulates—is not as efficient as the fabric filter, McKenna said. He also pointed out that in some cases of fly ash scrubbing or where there is acid in the gas stream, even the cost of equipment would be higher than for fabric filters. This is because special metals and materials would be required in the construction of the scrubber.

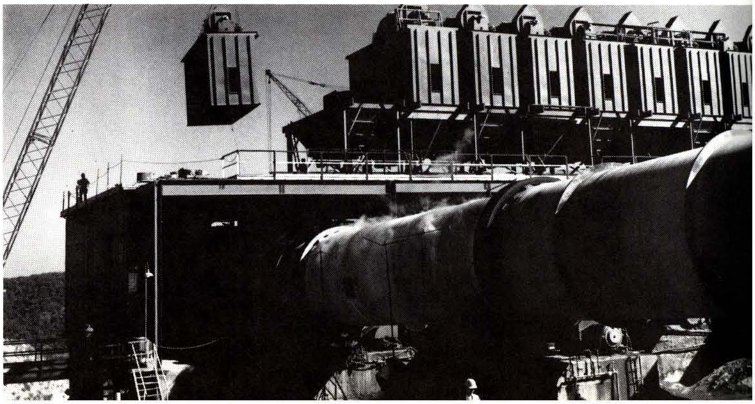
McKenna said electrostatic precipitators are cost competitive with fabric filters in such large projects as power plants. But, he added, the precipitators are not competitive on a smaller scale, such as would be suitable for an industrial boiler. Also, the cost of electrostatic precipitators increases greatly as additional equipment is added to achieve efficiencies of 99.9%. As codes and standards tighten up, efficiency will more and more be at a premium. "With this in mind, fabric filters become the way to go," McKenna said.

### Needed research

On a final note, Knowlton J. Caplan, University of Minnesota, outlined four areas where additional research is needed to help perfect fabric filtration. The first concerned the mechanism of "bleeding" or "seepage" where after a period of time, particles begin collecting on the clean side, or outside, of the filter bags in defiance of classical filtration theory.

Caplan also said in-stack sampling, shaking speeds and bag accelerations, and the electrostatic phenomenon, all need further study. Electrostatics is an especially important area of consideration because explosions can result on a large enough scale to destroy entire plants, he said. The problem arises from the fact electrostatics is difficult to measure and the bags are difficult to ground, Caplan told the symposium. Such research is increasingly of interest to manufacturers, Caplan said, because the market for such equipment is growing at a rapid rate. WSF

**Baghouses.** *New baghouses greatly reduced particulates at this cement plant*



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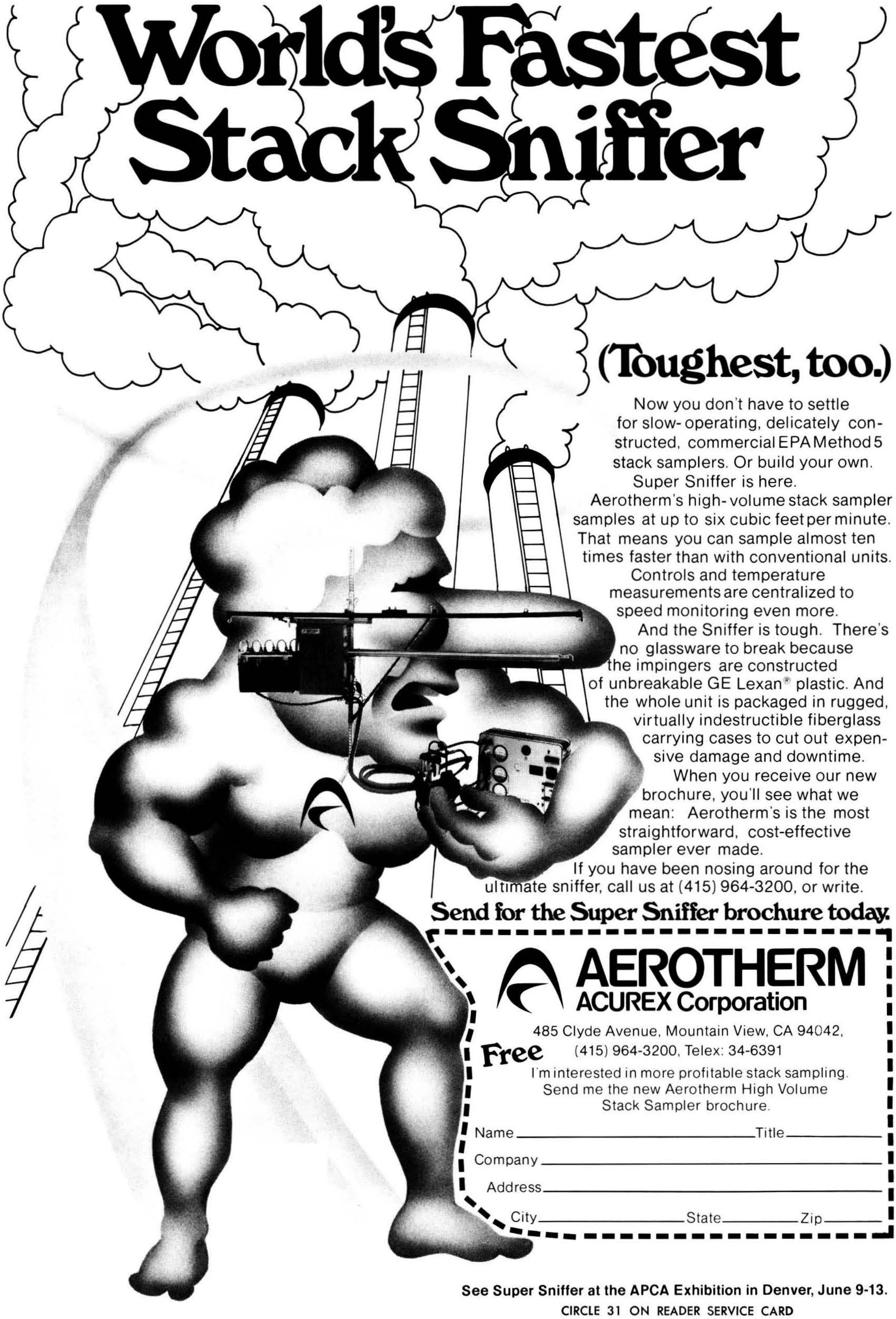

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CIRCLE 31 ON READER SERVICE CARD

Cleaner air and a new industry may both appear if pilot tests check out the technology of . . . .

# Cleaning coal by solvent refining

To scrub or not to scrub, that is the question.

Whether 'tis more economical and efficient to remove particulates and $SO_2$ from the end of the stack after the burning of coal,

Or to clean coal before it is consigned to the flames,

And thus, obviate the need for elaborate precipitator and scrubber installation . . .

So goes a major choice in the great coal burning debate. With enhanced technology, both principal routes may well be open. In any discussion of removal of potential air pollutants from coal, however, solvent refined coal (SRC) is receiving prominent consideration.

The principles of SRC were known since October 1932, when Alfred Pott and Hans Broche were granted a U.S. patent. However, it was not until 1964 that Pittsburgh and Midway Coal Co. (PAMCO, now a subsidiary of Gulf Oil), first started working with the U.S. Department of the Interior's Office of Coal Research (OCR) to determine the technical feasibility of SRC on a pilot scale.

### Pilot plants

SRC work has progressed to the point at which different groups have built, or are completing pilot plants. One such group is PAMCO, under OCR contract, which began construction of a $18 million, 30–50-tpd pilot plant near Tacoma, Wash., in December 1972. The plant should start up in the summer of 1974; it was designed by Rust Engineering Co., a subsidiary of Wheelabrator-Frye, Inc. A second (all-industry) group consists of Southern Services, Inc. (SSI, Birmingham, Ala., a part of Southern Co.), and the Edison Electric Institute (EEI). The latter is now operating a 6-tpd pilot plant at Wilsonville, Ala., designed and built by Catalytic, Inc. EEI funding for this plant has been assumed by the Electric Power Research Institute (EPRI).

In the SSI process, now being "shaken down," Western Kentucky 14 coal containing about 3% sulfur (S) is slurried in an anthracene oil-type solvent. About 95% of the carbonaceous material is dissolved. Hydrogen ($H_2$) is added under pressure, and the slurry is heated to about 750–850°F. The material is then subjected to pressures of 1800 psig, generally (although sometimes as high as 2800 psig), and $H_2$, hydrocarbon gases, water, and hydrogen sulfide ($H_2S$, made from organic sulfur in the coal), are separated. The $H_2S$ is reacted with sodium hydroxide and water to make sodium sulfide; however, commercially, $H_2S$ would be broken down to recyclable $H_2$ and marketable elemental S.

At this point, the pressure is decreased to 150 psi, at 600°F, to separate other gases, including remaining hydrocarbon values. After this step, the material contains solvent, dissolved coal, undissolved coal, and inorganics which would become $SO_2$ and ash if the raw coal were burned. Among these inorganics is pyritic sulfur, a major $SO_2$ source. The solid material is strained out through a Swiss "Funda" filter at 600°F so that low solvent viscosity and a high filtering rate may be maintained. Filtered solids are being stored for additional analytical tests.

Then the filtrate is warmed to 750°F in a vacuum column preheater, and the solvent is stripped off under 2 psia pressure and recycled to the plant. The distillation residue is SRC liquid; it is brought to 600°F and poured into water by a vibrating conveyor. The resulting solidified SRC, a clean, black, brittle material, minus virtually all ash and pyritic S, and over 60% of the organic S, is then drained.

Groundbreaking for the SSI pilot plant began in November 1972; construction was completed in September 1973. First runs were made this January. By mid-April, about 350 hr of operations were logged. The plant cost slightly less than $4 million.

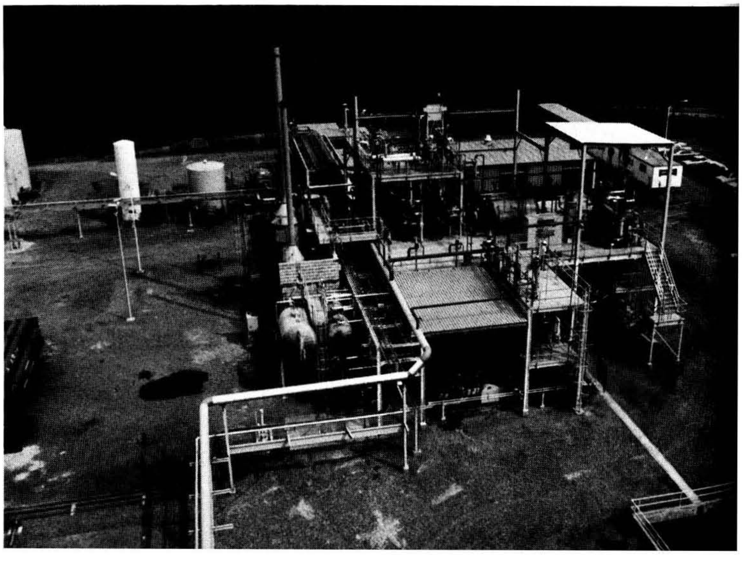
### Optimism

SSI project manager Everett Huffman is optimistic about the future for SRC. His optimism might not be without foundation.

First of all, SRC's heat value is about 16,000 Btu/lb; by comparison, raw coal's heat value generally ranges between 11,500–12,000 Btu/lb. Second, with solvent and filter treatment, coal of 2.5%, 5%, or even 7% S could be reduced to 0.9% S, or perhaps as low as 0.5% S; and from 8–20% ash to 0.166% ash. Such coal could meet EPA requirements for particulate and $SO_2$ emissions, especially in view of its higher Btu value.

Third, use of SRC might obviate or reduce needs for precipitators and scrubbers, which could have high capital costs, and, under the present state-of-the-art, a 5–8% energy penalty. Moreover, the level of technological advancement of such devices is a subject of spirited debate in many quarters, as is its potential for water or land pollution. On the other hand, purchase of SRC is an operational expense which can be "written off" in the year incurred, and use of SRC

**Pilot plant.** *This year, this 6-tpd pilot plant in Alabama started operating.*



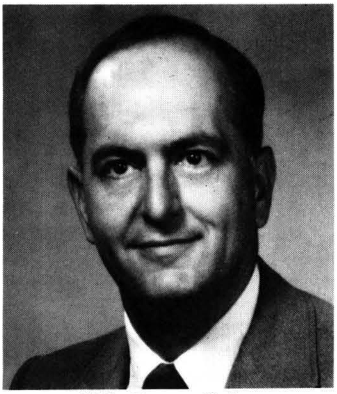
should involve no installation and maintenance of elaborate capital equipment, according to one engineering and economic view recently expressed.

Huffman said that it is a bit premature to peg dollar figures on SRC economics at this time. He did, however, mention a few material figures. For example, it is expected that the SRC process will use 1.5–2.5% $H_2$ (of the total weight of coal). Liquefaction and gasification techniques require considerably more $H_2$, as well as more rigorous conditions of temperature and pressure. Therefore a material and energy saving could be realized.

The SRC process would spin off certain by-products which may be useful. One such by-product would be elemental S, recovered from organic and pyritic sources in the raw coal. A second would be hydrocarbon values which might be recovered and sold or recycled into the plant as an energy source. There may also be other useful mineral values in the solids removed; and the solvent itself, which can replace small losses sometimes incurred in the SRC process, is generated from the raw coal. Yet another benefit may be realized if the 5% of the coal, which remains undissolved in the solvent and is filtered out, could be economically gasified to produce energy for the SRC plant and its ancillary facilities.

**Matters under study**

One of the prime reasons for the SSI pilot effort was to determine the best method of removing solids (potential ash and particulates) from SRC. Filtering seems to remove enough solids so that as little as 0.1% solids may remain in the filtrate. However, hydrocycloning (hydrocloning), to be tried at the Tacoma, Wash., pilot plant could prove less expensive and more easily installable and maintainable than the filter scheme. Consolidation Coal Co. (Consol) tried hydrocloning on a small scale, but indications were that 1% solids may remain in what corresponds to a filtrate.

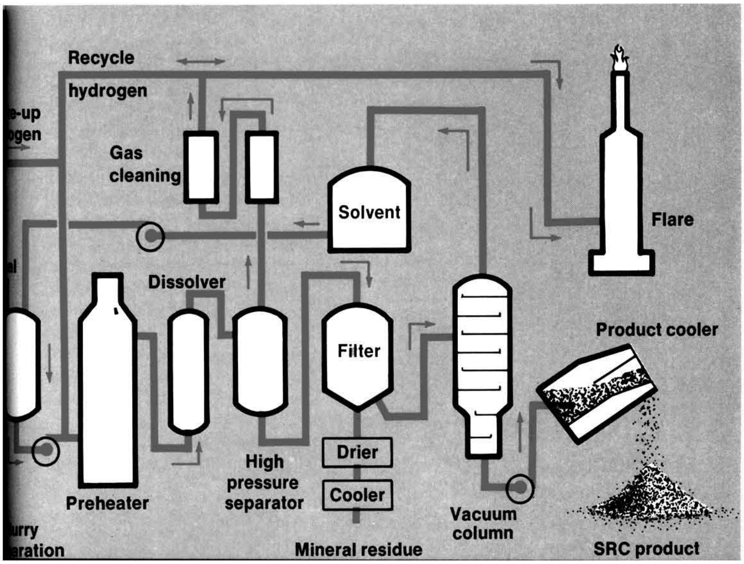


SSI's Everett Huffman

Another matter under study is the most rational way of handling the removed solids. One objective is to avoid having solid wastes; another aim is to prevent disposal in water that would cause a pollution problem similar to acid mine drainage. Under consideration is gasification of the carbonaceous material, during which $H_2S$ would be produced from the iron pyrites. S would be recovered from the $H_2S$; $H_2$ would be recycled to the plant, as would the gas product. Other by-product values would be ascertained.

Finally, how should the SRC itself be handled? If a customer is very near an SRC plant, the SRC could be supplied as a liquid. The other course is to solidify it, and front runners among approaches under consideration are the Sandvik belt (looked at by SSI) and the prilling tower (PAMCO/OCR/Rust). The Sandvik belt is of stainless steel and is cooled underneath by water. Liquid SRC would freeze on the belt and flake off. In the prilling tower, liquid SRC falls from top to bottom and solidifies on the way down.

*Here is the schematic diagram which shows how it works*



**Prospectives**

If the results of the SSI and PAMCO pilot tests justify the present optimism, Old Ben Coal (subsidiary of Standard Oil of Ohio), together with Toledo Edison would start a $75-million, 5½-year project for a 900-tpd demonstration plant. The plant would be designed and built by Catalytic, Inc. Some components of the plant, however, would work under the more vigorous temperatures and pressures associated with liquefaction. Thus, although the plant would be an SRC facility, it would also be a two-pronged enterprise involving coal liquefaction.

For the future, Catalytic, Inc. looks to the possibility of a 20,000-tpd commercial SRC plant. Cost of such a plant is estimated at $200 million, but clean coal and by-product values, as well as solvent, hydrogen, and hydrocarbon recycling potential, and expected operational economy could be redeeming features.

SSI's Huffman cautions that while SRC shows real promise, it should not be regarded as "the answer to a maiden's prayer"—nor should any other technique be so regarded. From the standpoint of using coal and safeguarding environmental quality, a whole technical "bag of tricks" will have to be evolved. This bag of tricks will include improved coal liquefaction and gasification methods, as well as better gas cleaning at the end of the pipe; either approach would not only be more economical and efficient, but would be a source of useful by-products also. The evolution of these parallel approaches will proceed apace with the development of SRC. This is certainly understandable, since the demand for gas and liquid products and fuels will remain high.

In the long term, SRC could offer new prospects for those electric utilities needing to burn coal and meet clean air standards, and to avoid use of petroleum products or natural gas. Indeed, if SRC technology measures up to expectations, perhaps a new clean fuel and chemical industry will appear on the American scene—a coal refining industry. JJ

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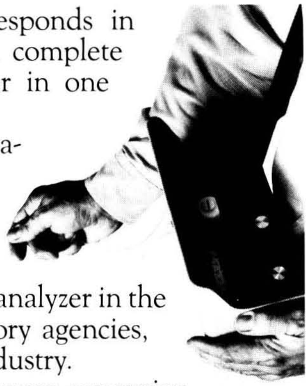

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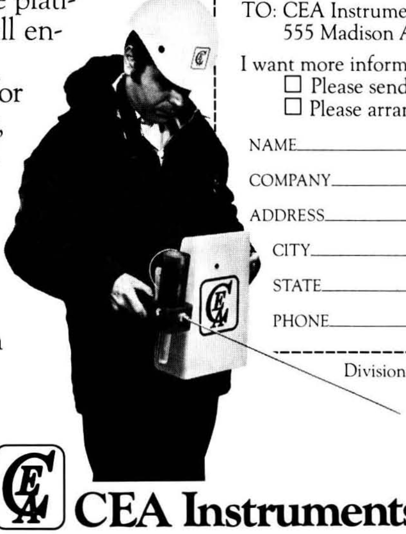

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CIRCLE 17 ON READER SERVICE CARD

# WWEMA shows how to clean water

## Industry wants to know that heavy financial outlays and technological commitments for compliance with BPCTCA rules will not be an exercise in early obsolescence

Sixty-six years old this year, the Water and Wastewater Equipment Manufacturers Association (WWEMA) took the occasion of its second industrial pollution control conference and exposition (Detroit, Mich.), held in April, to remind industry that the July 1, 1977, water cleanup milestone date is drawing closer. On that date, according to the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500), industries discharging effluents to navigable waters must abate pollution by means of the "best practicable control technology currently available" (BPCTCA). Thus, BPCTCA was the theme of WWEMA's conference and exposition, attended by over 2200 persons.

How will industry meet the BPCTCA requirements in order to obtain and maintain discharge permits? The more than 300 companies which are members of WWEMA are being looked to for tangible answers to this urgent question. Some of these possible tangible answers were shown by 83 exhibitors who attended the WWEMA industrial show. Others were suggested in the 87 papers presented at the technical sessions by representatives of industry, government, and the academic.

David Gallagher, WWEMA's executive director, said that WWEMA is eager to cooperate with the EPA to arrive at a workable decision as to how industry will go to achieve water cleanup goals.

### Some negative thoughts

Some impressions concerning what could be impediments to progress in pollution control have been aired frequently in the past, and were discussed at the conference's general session. These include:

- uncertainties and changes in federal regulatory and enforcement practice
- assumptions that significant new technologies would have a major impact upon the cost and benefit of compliance
- impractical short-term and long-term goals which may tend to include the very practices that have caused pollution in the past.

Robert Bruns, president of International Hydronics Corp., said that these impediments date back to 1965. Many of them, he explained, stemmed from shifts in the federal establishment, and were exacerbated by the unrealism of the goals themselves. The "illusory promise of technological advance in time to ease things" was another contributor to the general malaise.

Speaking in a private capacity, Edward Bryan of the National Science Foundation termed this malaise understandable, partly because of unrealistic promises of higher benefit at lower cost, and partly because of technocratically fostered optimism which can cause a credibility gap. However, Bryan pointed out that industry wants to be responsive to environmental needs, but needs assurances that capital investments and technological commitments, which could become rather heavy and involved, will not be wasted because of rapid obsolescence. Bryan also brought forth the idea that industry is far less interested in what is promised than in what can actually be delivered.

Glen Pratt, chief technical coordinator for the U.S. EPA/Chicago (Region V), noted that while there may be uncertainties from the technological standpoint, still, some degree of technological forecasting is necessary to formulate effluent standards that theoretically should be met if BPCTCA is applied. These standards will have to be met if an organization is to obtain and maintain a valid discharge permit, which all dischargers are supposed to have by December 31, 1974. Actually, the December 31 goal is unattainable, in Pratt's opinion; thus, major permits will be issued by that date, with the remainder in force by May 1975. It is interesting whether the lack of a discharge permit, attributable to this time slippage, might be a legal defense for dischargers faced with court action during this interim period.

**WWEMA's Gallagher**
*Wants to cooperate with EPA*

Industry's worries concerning the 1977, as well as the 1983 compliance dates, were not lost on Congress. Thus, Congress created the National Commission on Water Quality (NCWQ), chaired by former Governor Nelson Rockefeller of New York, to study and determine socioeconomic and environmental effects of attaining, or not attaining 1977 and 1983 goals. The NCWQ's pamphlet, "Study plans," is profitable reading, and those interested should write to the National Commission on Water Quality, P.O. Box 19266, Washington, D.C. 20036.

### Working toward BPCTCA

Many companies nevertheless are going ahead full speed toward development, fabrication, and installation of BPCTCA. This effort involves many approaches—adsorption, aeration, biological techniques, filtration, flotation, ion exchange, ozonation, physical-chemical methods, reverse osmosis, and water recycling, among other means of attack.

For example, the Wayne H. Coloney Co., Inc. (Tallahassee, Fla.) worked on the problem of oily waste from a bus and truck washing and cleaning operation with dried bacteria cultures (*ES&T,* March 1974, p 196). After considerable experimentation and engineering work, BOD reduction of 97%, COD reduction of 98%, total and suspended solids reduction of 95% and 98%, respectively, and oil and grease reduction of 95% were realized. Shock loads could be handled.

The process was granted a permanent operating permit by the Dept. of Pollution Control, State of Florida. However, this permit expires June 6, 1977. Total capital costs, including all "extras" needed to optimize the system, were about $15,000, with operating costs near $10/day. This is much less than capital costs for "conventional" equipment, which could be at least $62,500, with operating costs near \$10,000/year (about \$28/day).

Wayne Coloney, the company's president, said that for maximum results, a cooperating four-member team, consisting of the facility owner, the bacteria supplier, the system builder, and the design engineer, is needed, as well as carefully controlled, regular application after thorough experimentation to ascertain the proper bacteria type and dosage.

Victor F. Weaver, Inc. (New Holland, Pa.), a large poultry processor, decided to install its own 1.5-mgd wastewater treatment plant when the municipal plant became overloaded and ineffective. Principal problems were hydraulic load and BOD; the latter was rarely less than 1000 ppm. Weaver opted for a first-class treatment plant, with virtual duplication of all equipment selected. For the discharge permit to be granted, future drinking water potential for the stream receiving the effluent had to be taken into account, as well as BOD, ammonia, and nitrate nitrogen.

To receive and process primary treatment effluent, the Weaver treatment plant is mainly an aeration, clarification, and flotation system. After the system was in operation for 60 days, final BOD discharge was down to 30 ppm. The plant effluent (about 850,000 gpd), consisting, of 1.5% solids, is made into a sludge of about 6% solids by addition of iron salts, lime, and polymer. The goal, however, is to get to 50% solids, or better, to ease mechanical handling, and to make a product more acceptable for preparing animal feed.

Costs come to \$1.2 million with a \$100,000 annual savings after a 10-year debt retirement. If the pretreatment route had been taken it would have cost \$500,000 to eliminate a sewage surcharge levy.

Subsurface Disposal Corp. (SDC) discussed experiences with deep-well industrial waste disposal. According to SDC, about 280 wastewater injection wells have been constructed in the U.S.; approximately 180 of these are operating. The current average increase in the number of new wells is 30 per year.

Disposal wells are used because there is no feasible alternative; the disposal method is a positive one and is economical, with minimal operational costs, in SDC's view. Such wells can have occasional problems with injection zone plugging stemming from various causes; however, such problems can be obviated by proper design, and the wells should give years of reliable service, according to SDC. Nevertheless, rigorous care must be taken with design, construction, testing, and record keeping so the freedom from problems and their concomitant cost heartaches may be maximized.

Many other timely papers were presented by representatives of companies of all sizes, and covered almost the whole gamut of water pollution monitoring and control methods and water recycling and resource recovery techniques.

**The air-water interface**

What happens when one type of pollution abatement creates another pollution problem? Howard Hesketh of Southern Illinois University (Carbondale, Ill.) discussed how this question arose at a Mitsui Co. aluminum plant in Japan, and how Chemico, Inc. of New York provided technology for an answer.

### Partial list of exhibitors

Abcor, Inc.
Air Products & Chemicals, Inc.
APCO Valve & Primer Corp.
Bausch & Lomb, Inc.
Crane Packing Co.
Degremont Inc.
De Laval Separator Co.
Delta Scientific Corp.
Du Pont, Instrument Products Div.
Ecodyne Corp.
Ecologic Instrument Corp.
Edo Corp.
Envirex, a Rexnord Co.
Envirotech Corp.
FMC Corp., Environmental Equipment Division
The Foxboro Co.
Golden-Anderson Valve Specialty Co.
Goodyear Tire & Rubber Co.
Gorman-Rupp Co.
W. R. Grace & Co.
Hach Chemical Co.
Hercules, Inc., and its subsidiary company, AWT Systems, Inc.
Honeywell
Industrial Control Systems, Inc.
International Hydronics
Komline-Sanderson
Laval Separator Corp.
Leeds & Northrup Co.
Met-Pro Systems
Neptune Microfloc, Inc., Div. of Neptune Meter Co.
Nichols Engineering & Research Corp., Div. of Neptune Meter Co.
Orion Research Inc.
The Pantasote Co.
The Permutit Co.
Pro-Tech, Inc.
RobertShaw Controls Co., Industrial Instrumentation Div.
Sigmamotor, Inc.
SWECO, Inc.
Swift & Co.
Union Carbide Corp.
Wallace & Tiernan Division, Pennwalt Corp.
Westinghouse Electric Corp.
Wheelabrator-Frye, Inc., Water and Wastewater Div.
The Rust Engineering Co.
Zurn Industries, Inc., Enviro Systems Div.

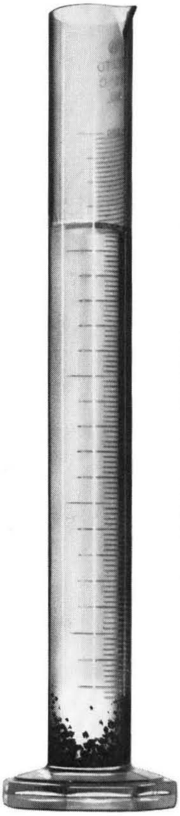
Mitsui has a 156-MW boiler which emits $SO_2$ that has to be scrubbed. The scrubber process, however, must not itself create a water pollution or solid waste problem while treating the $SO_2$. Thus, after waste gases are properly conditioned in an electrostatic precipitator, they are scrubbed by an open-throated venturi device. Lime is the scrubbant, and is conveniently available as carbide sludge (normally a pollution problem itself) from a nearby acetylene plant.

After $SO_2$ scrubbing, the reacted lime and the products are slurried to settling ponds lined with polyethylene to prevent water pollution caused by leaching into soil. The solids quickly settle; the liquor is percolated through fly ash, becomes clear water with small, easily made-up losses, and is recycled to the plant or safely discharged in case of excess.

**From A to Z**

The WWEMA exposition, in which companies from A to Z (Abcor to Zurn) displayed a whole variety of items ranging from small monitoring instruments and specialized systems and products to replicas of large-scale total systems, provided a tangible, visual idea of the possible courses that the development of BPCTA will take. Among the concerns showing large industrial systems were Ecodyne Corp., Sybron Corp./Permutit, Union Carbide, Wheelabrator-Frye, and Zurn Industries, Inc. Instruments and special systems and materials were shown by companies such as Abcor, Ecologic Instrument Corp., Goodyear, Hach Chemical Co., and Pro-Tech, Inc. One relative newcomer was Edo Corp. (College Point, N.Y.), with a Doppler flowmeter for monitoring; Edo is widely known as a maker of equipment for oceanographic sonar transducers and recorders and related devices.

Thus, there may be numerous approaches available as far as meeting BPCTCA requirements are concerned. Nonetheless, progress would be markedly enhanced in timely fashion if industry's apprehensions, as described earlier, could be speedily and realistically resolved and put to rest. JJ



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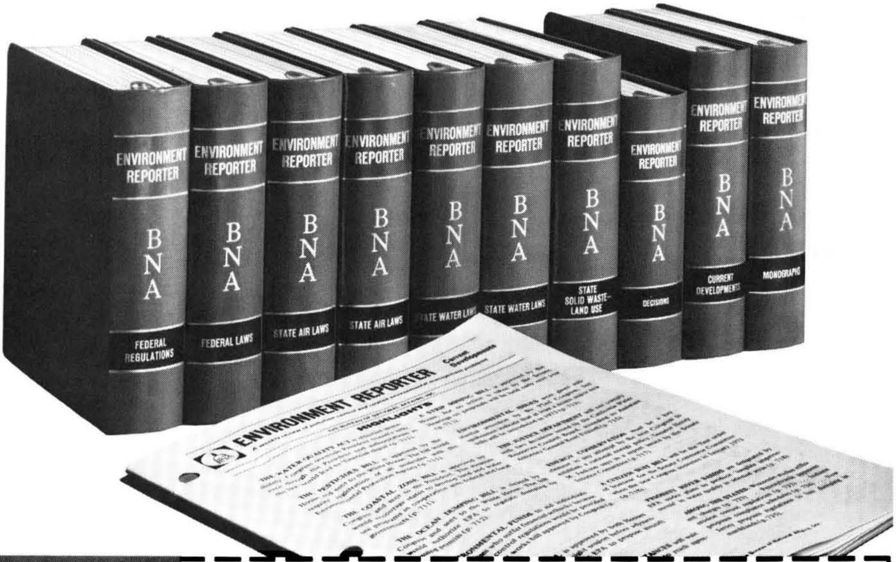

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CIRCLE 40 ON READER SERVICE CARD

# The largest U.S. wet scrubber system

## At the Four Corners plant, Arizona Public Service Co. is not leaving any corner unturned in its search for stack gas controls for power production

Out in the desert in the southwest portion of the U.S. near where four states come together is the Four Corners power plant. The actual plant is located on the Navajo Indian Reservation, about 20 miles west of Farmington, N.M. All told there are five power generating units at this location with a generating capacity of nearly 2.1 million kW. All units are coal fired, the coal being supplied by Utah International, Inc., in its surface mining operation on the Navajo Indian Reservation.

What makes this plant unique is the fact that emission control systems have been installed on all the units, but more controls—costing an estimated $158 million—will be added to meet the "moving target" of newer air quality standards proposed by the State of New Mexico and the Environmental Protection Agency. The experience of Arizona Public Service Co. (APS), the plant's operator, with so-called reliable and available technology is noteworthy. Despite considerable setbacks, APS continues to get the bugs out of such reliable and available controls. They haven't given up yet. Their experience serves as an example to others.

Controls for particulate matter have been installed on the larger units 4 and 5; yet others are to be added. For example, Research-Cottrell electrostatic precipitators were installed on unit 4 in July 1969 and on unit 5 by July 1970 when the units were constructed. These precipitators cost nearly $6 million; they were designed for 97% removal of fly ash. Their removal efficiency was verified by Truesdail Lab (Los Angeles, Calif.).

Since the installation of these controls, which are in actual operation on a day-to-day basis, there have been only two violations of New Mexico air pollution codes, once with both units on July 18 and 19, 1972, and again with one unit in November 1973.

Electrostatic precipitators were also considered for units 1, 2, and 3, but removal efficiencies would not satisfy existing codes even as late as 1971. Chemico wet scrubbers were installed on units 1, 2, and 3; they became operational in December 1971. While designed only for fly ash removal, test results of York Research, the EPA, and the State of New Mexico confirmed that the units were also removing 30–35% of the $SO_2$ emissions from the coal-burning units. The scrubbers met efficiency guarantees and met all codes in existence for fly ash removal.

Lyman Mundth, vice-president—power production of APS, told *ES&T* that the utility has experienced difficulties with the scrubber control devices but in no way does APS intend to give up on controls.

### The moving target

But neither these control devices nor the removal efficiencies are good enough in this continuing age of moving targets. The federal EPA late in March said that by July 31, 1977, 70% of the $SO_2$ emissions from the plant's four stacks (units 1 and 2 have a common stack) must be removed.

A new regulation on particulate matter has been issued by the State of New Mexico to become effective December 31, 1974. This new requirement means supplementing present controls on units 4 and 5. For example, particulate emission control for units 4 and 5 would have to be increased from 97% fly ash removal efficiency to 99.74% efficiency. And then in order to comply with the federal EPA requirement of 70% $SO_2$ removal efficiency, an $SO_2$ absorption removal system would have to be installed downside of the precipitators—a scrubber system the owners intend installing on units 4 and 5. Present estimated cost of the scrubbers and $SO_2$ removal system is $140 million. Of course, scrubber $SO_2$ removal efficiency in units 1, 2, and 3 would have to be upgraded to 70% too, from 30–35%. Estimated cost of this upgrading is $18 million.

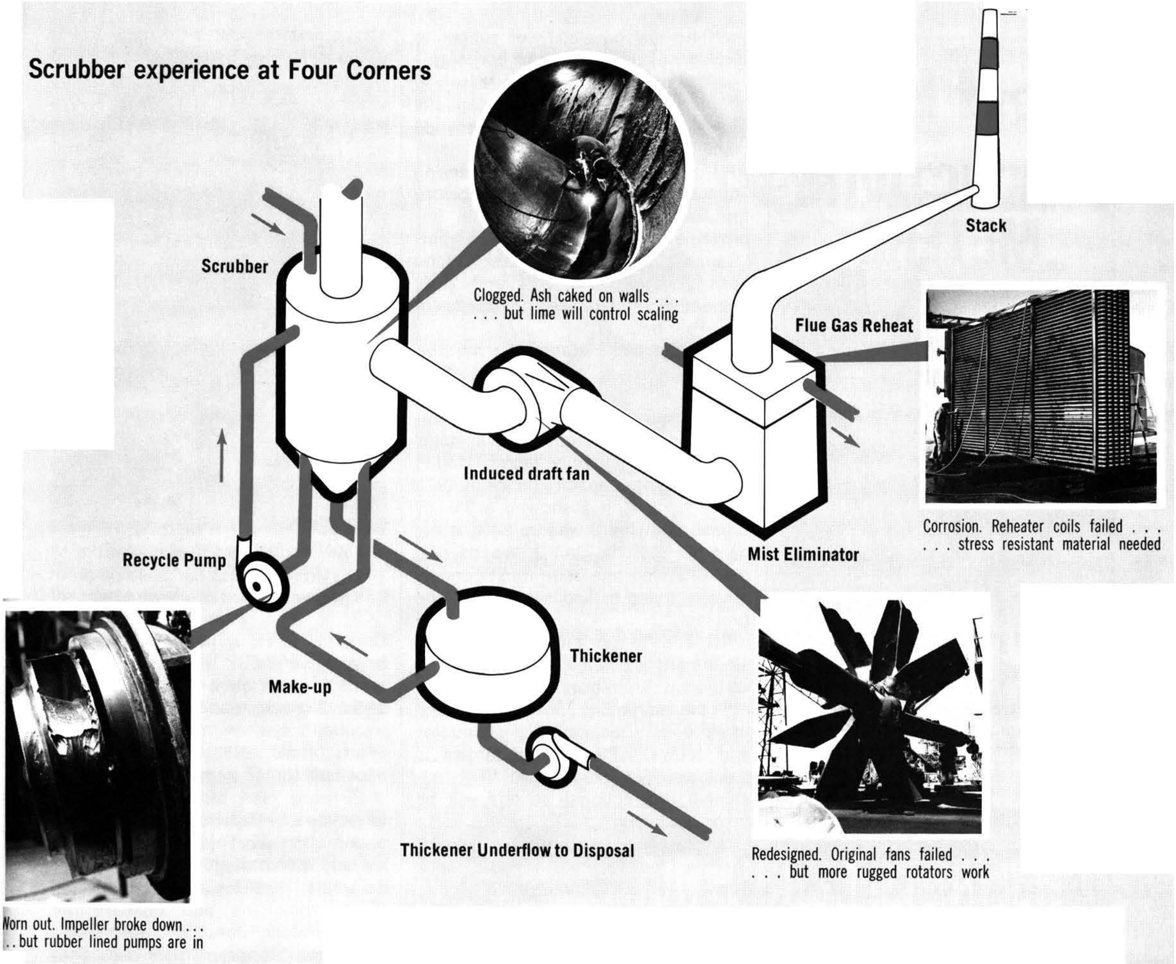
Lyman Mundth said that the additional controls for units 4 and 5 were recommended by Bechtel Corp., the San Francisco-based consulting firm with enormous electric utilities experience. APS is going full steam with these controls.

If limestone is used in the $SO_2$ removal process by APS, an estimated 400–500 tons of limestone would be needed each day. At present, the consulting firm of Dames & Moore is making a survey of lime and limestone availability for APS. There are six limestone deposits within a few hundred miles of the plant. The utility needs a 35-year supply!

Lyman Mundth said that APS plans to be in the business of power production at the Four Corners plant for a long time. He explained that the utility has a 35-year agreement with Utah International for the coal supply. Bill Grant, spokesman for Utah International says that its area of coal mining today would last 125 years at the present rate of coal consumption at the Four Corners plant. The plant burns about 25,000 tons per day.

Nevertheless, the plans and actual experience do not go hand in hand. Plant manager Walker Ekstrom of the Four Corners plant explained that the plant is a base load power plant with a high-capacity factor, meaning that the fuel—the surface-mined coal—is cheap, and the goal of the plant is maintenance of the highest availability of power production with limited outages.

However, the maintenance costs are high. Ekstrom explained that the ash content of the coal is 22%—one


Scrubber experience at Four Corners

Clogged. Ash caked on walls . . .
. . . but lime will control scaling

Corrosion. Reheater coils failed . . .
. . . stress resistant material needed

Redesigned. Original fans failed . . .
. . . but more rugged rotators work

Worn out. Impeller broke down . . .
. . but rubber lined pumps are in

of the highest ash contents of any coal in the U.S.—and that the ash is very abrasive on plant equipment.

Each unit at Four Corners is shut down for scheduled outage once a year. During this outage normal and routine repair and replacement of equipment are performed. But, he pointed out that the operation of the wet scrubbers has caused more delays and maintenance of equipment. Ekstrom said that in 1973, the first full year of scrubber operation on units 1, 2, and 3, it was necessary to add 15 to 20 people to the maintenance department which in prescrubber days operated at slightly more than 100 people.

### Getting the bugs out

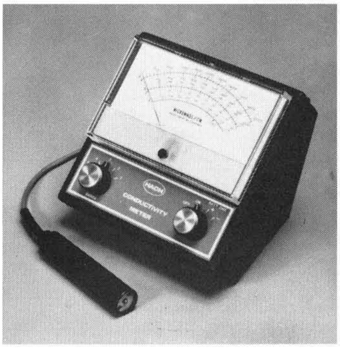
The scrubbers have been plagued by numerous problems which have created other than routinely scheduled outages. "It must be remembered that this system reflects 1969 technology, was the first of this magnitude, and that a lot of lessons have been learned and are being applied," said Robert Blinckmann, vice-president and general manager of Chemico Air Pollution Control Co. "Since the initial start-up, Chemico has worked with APS to solve the problems encountered."

Some of the original recycle pumps had to be replaced after only 700 hr of operation because they wore out. APS tried using six different pumps made of as many types of alloys in order to overcome the abrasion which was damaging the pumps. None of the six pumps worked well, so APS has been testing a rubber-lined pump which now has operated successfully for more than 4500 hr. Originally, rubber-lined pumps for this application simply were not available.

Scaling of the scrubber led to clogging problems and other downtimes. All six of the induced draft fans failed and had to be replaced. The original fans were installed December 1971 and cost about $1 million. The replacements were of a new, more rugged design and utilized Inconel for greater strength.

But the most serious and perhaps most expensive experience to date is the problem of stack gas reheat coils. Normally, the stack gas is heated with steam coils to raise the temperature of the flue gas above condensation temperature to avoid condensation in the stack and breeching. Heating of the gas also expands the gas, giving it more buoyance so it rises faster and higher and is more readily dispersed in the air.

Ekstrom said it would take several million dollars to replace these reheat coils if a material could be found with greater resistance to stress corrosion, but none has been found yet. The coils were out of service when *ES&T* visited. The two stacks for units 1, 2, and 3 have been coated with a protective material, Stak Fas. These units now operate with wet stacks. Custodis Construction Co. (Chicago) completely removed the brick lining from the stacks, washed the chimneys with acid and sprayed on a $\frac{3}{16}$-in. layer of the protective material. Chemico and APS are studying other alternatives



such as the possibility of reheating stack gases directly with oil burners.

It all adds up to a basic lesson in economics. In 1972, the capacity factor of units 1, 2, and 3 declined considerably from prescrubber days. APS vice-president of engineering Thomas G. Woods, Jr., said before the New Mexico Environmental Improvement Board last December, "Capacity factors for each of the units dropped 13%, 8%, and 29%, respectively, compared to prescrubber experience."

Much of this reduction is attributable directly to the induced draft fans. Since they were replaced in 1972, there has been a marked improvement in scrubber availability and in plant capacity factor. Unit 1 had the same capacity factor in 1973 as in 1972. Unit 2 showed a 3% increase and Unit 3 was up 34%, a net gain of +5% for Unit 3. Woods said that Chemico has been most cooperative in trying to find solutions to the problem.

To add to all the materials and equipment problems, it cost APS an estimated $1 million a year to operate the scrubbing controls on the three units. Despite all the troubles and delays, APS has not thrown in the towel. For example, in 1974, additional, correctional actions will be taken, including:

- replacing the remaining original recycle pumps with rubber-lined pumps
- adding a permanent lime-feeding device to control the degree of scaling and buildup of sulfates and sulfites throughout the scrubber system.

In 1974, APS will begin sharing the output of the Navajo Power Plant (Page, Ariz.), another coal-fired station. It will be equipped with "hot side" electrostatic precipitators of Western Precipitation, a division of Joy Mfg. Co.

### What about monitoring

Just 10 miles north of the Four Corners plant is the San Juan power plant which is jointly owned by the Public Service Co. of New Mexico and Tucson Gas and Electric Co., which are cooperating with the Four Corners plant owners in an air-monitoring program for the area.

All told, the plants' owners have invested about $300,000 in that program. They have eight monitoring stations in the area. The companies intend keeping emissions at a level which meets the national air quality standard and keeping a record of emissions. Four ambient air monitors were installed in 1972, another four a year later, in the spring of 1973. A weather tower was added at Four Corners in May 1973. The cost breakdown shows a $200,000 investment for the eight monitors (about $25,000 each) and $60,000 for the weather station. The companies spend about $65,000 on operating expenses for the monitoring.

**APS vice-president Mundth**
*The company has not given up on power plant emission controls*

Recently, the companies elected to go the contract route for the evaluation and reporting of their monitoring and meteorological data. Western Scientific Service (Fort Collins, Colo.) maintains and collects the data from the weather tower. Sierra Research (Boulder, Colo.) does likewise for the monitoring data from the eight monitors. Loren Crow, a consultant from Denver, advised the firms on the placement of the monitors. They are scattered in a circle around the two power plants. Intercomp (Houston, Tex.) has a diffusion model; the monitoring data are fed into the model to see if any violations of standards occur.

In addition, the Four Corners plant owners added an on-site environmental laboratory at an expense of $65,000, budgeted $50,000 in 1974 for testing which required a continuous 2–3 people effort, and has instrument repair personnel on hand. A full test of an electrostatic precipitator may run as much as $50,000; normally it takes four people three days to test a unit.

In 1974, continuous stack monitors for $SO_2$ and $NO_x$ emissions will be installed on units 4 and 5, APS says. The installation of such stack gas-monitoring systems entails an additional investment of $93,000.

Again, in this age of environmental moving targets it is useful to point out facts. In its implementation plan, which was submitted to the federal EPA, the State of New Mexico required that the Four Corners plant install a continuous stack gas monitoring system but that portion of the plan was disapproved by EPA!

Keeping up their environmental guard on another area, the owners of Four Corners and those then planning San Juan contracted for a study of potential vegetation damage study with Dr. Clyde Hill of the University of Utah. The study has been continuing since 1971. In data for the past three years, Dr. Hill has found neither damage to alfalfa, the prime concern since the material is of commercial value, nor to other native species. His investigation involves more than 40 test plots; his main concern during the growing season is observation of young plants since they are potentially more susceptible to air pollution damage. The study is funded at the $50,000/year level by the owners of the Four Corners and San Juan power plants.

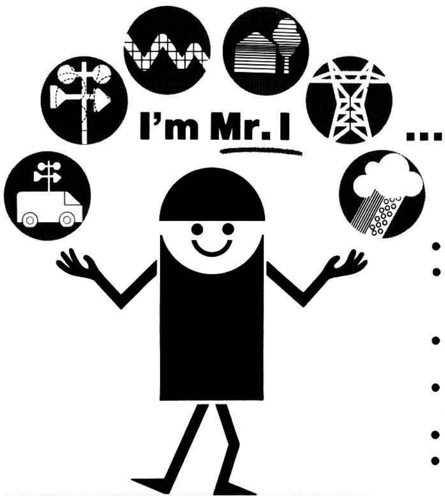
### Sludge problem unresolved

APS has a scrubber sludge disposal problem that is common with other scrubber-equipped power plants. At the Four Corners plant, the total ash production has been estimated to be 1.5 million tons per year; about 75% of which is returned to the mine by Utah International in its reclamation practice. But for the scrubber sludge, there is no apparent and immediate solution.

Mundth mentioned that APS is looking at the process of International Utilities/Conversion Systems, Inc. (*ES&T*, Oct. 1972, p 874) as well as the sludge disposal process of the Radian Corp. (Dallas, Tex.). Furthermore, APS has contracted for a study on how to dispose of this sludge with Stearns-Roger Corp. (Denver, Colo.). Results are forthcoming.

Arizona Public Service Co. represents a $1,003,218,000 investment. Total business for the company was $224,956,000, according to 1973 corporate figures (year ending December 1973). By the end of that period, APS had invested and authorized $133 million in environmental controls at its Four Corners and Cholla plants and spent in excess of $1 million a year on the operation of these controls.

During all of this costly testing and reduced capacity production, APS has requested and been granted two rate increases since 1970; a 6.3% rate increase became effective May 1973, and a 4.65% increase became effective in October 1973. Despite the troublesome experience, APS continues to seek reliable, efficient, and available controls. SSM



**Robert L. Chapman**
*Beckman Instruments, Inc., Fullerton, Calif. 92634*

# Continuous stack monitoring

## Commercial instrumentation is readily available for two of three basic approaches to EPA's stationary source requirements

The application of automatic instrumental monitoring systems to stationary sources has been feasible for many years but, due to their cost and the lack of any incentive, industry has ignored them. Recent activity on the part of the Environmental Protection Agency (EPA), and particularly the promulgation of requirements for the monitoring of certain pollutants, has stirred sudden interest in such systems. This interest has spurred the development of: new instrumental methods, specialized sample interface components and systems, and systems equivalent to the classical manual analytical techniques.

Attempts are being made to provide methods for testing instrument performance and expressing it in standard format. Once established, such standards will allow the specification of instrument performance requirements to the benefit of government agencies, instrument manufacturers, and users.

### Monitoring stationary sources

One of the most basic segments of air quality control is the control of pollutant emissions from stationary sources such as electric generating and industrial manufacturing plants. Since it is presently impractical to eliminate completely such emissions, controls consistent with available technology must be developed to provide a practical balance of priorities. With quantitative measurement techniques, the effectiveness of the controls can be checked by monitoring the performance of a plant for compliance under typical or peak production conditions, assuming that the plant continues to operate within the prescribed limits. However, it is advisable that the emission of certain critical pollutants be monitored on a continuing basis. This requires dependable instrumentation that can be located permanently at the points of emission.

Stack monitoring requirements for certain categories of new, or newly and substantially modified, plants are established by the EPA, and are promulgated as integral parts of the federal law governing the performance of such plants. Controls on old plants in the same categories are left to the jurisdiction of the individual states in which they are located.

In December 1971, standards of performance were established for the first five categories of new plants, including nitric acid and sulfuric acid plants. A note of clarification is needed regarding the monitoring of nitrogen oxides. The official definition of the term "nitrogen oxides" includes all oxides of nitrogen, except nitrous oxide, measurable by the phenoldisulfonic acid method. Essentially, this means the sum total of nitric oxide and nitrogen dioxide. The emission standards, however, are expressed in terms of nitrogen dioxide.

In the stack gases from solid and liquid fossil fuel combustion, virtually all of the nitrogen oxide is in the form of nitric oxide. In the case of gaseous fuel, some portion may be nitrogen dioxide. The EPA has proposed, therefore, that in the former case the measurement of nitric oxide alone is adequate, while in the case of gaseous fuel, both nitric oxide and nitrogen dioxide should be measured, either individually or in combination. The stack gas from nitric acid plants contains mixtures of nitric oxide and nitrogen dioxide in which the latter may amount to 10–50% or more of the total. Thus, both forms should be measured in this case, either individually or combined.

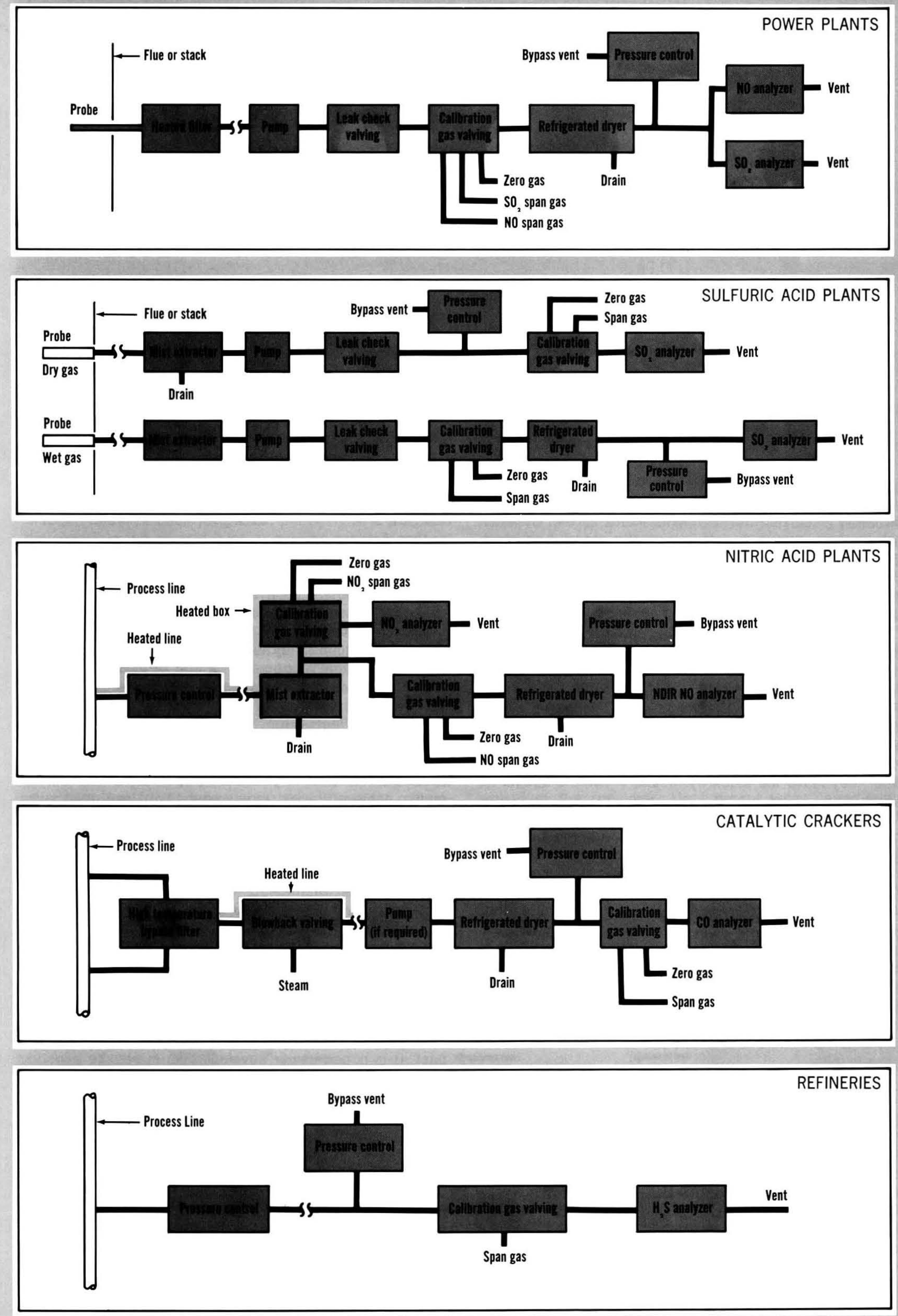
In April of 1973, asbestos, beryllium, and mercury were declared officially to be hazardous air pollutants and all plants and operations emitting appreciable quantities were placed under the control of the EPA. Emission standards were established and performance tests, utilizing filters and manual wet chemical techniques, were prescribed. No stack monitoring requirements were included, however.

In June 1973, proposed regulations governing seven more categories of plants were published. Only two of these categories require continuous monitoring—petroleum refineries and iron and steel plants. Within the refineries, only the fluid catalytic cracking unit, catalyst regeneration unit, process heaters, boilers, and waste gas disposal systems require monitoring. Within the iron and steel plants, only basic oxygen process furnaces are affected.

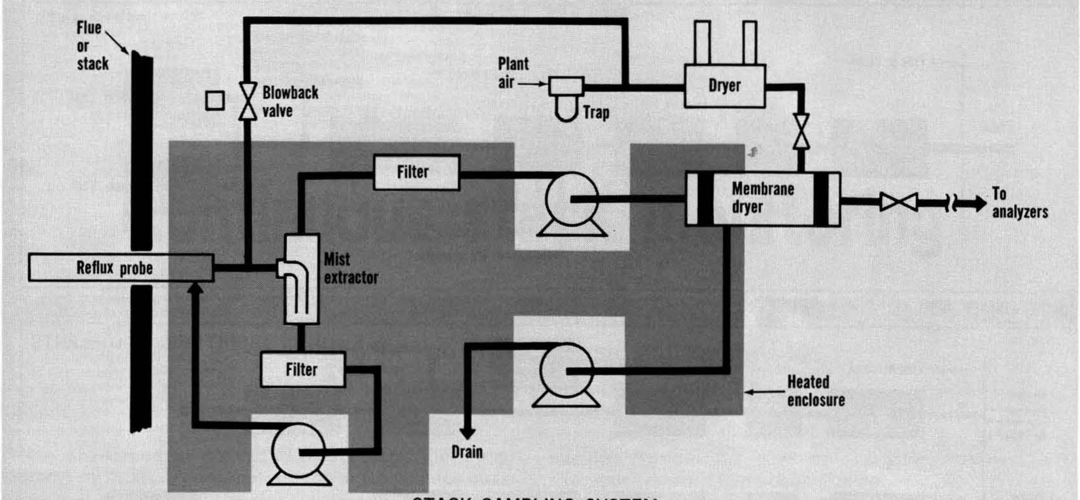
It should be noted, with respect to the requirements placed on heaters, boilers, and waste gas disposal systems in refineries, that the aim is to reduce the amount of sulfur dioxide emitted to the atmosphere. While this may be accomplished by either removing excess hydrogen sulfide from the fuel gases or by scrubbing excess sulfur dioxide from the combustion gas, it is expected that in essentially all cases, the former method will be used. Thus, compliance will be determined in most cases by determining the hydrogen sulfide content of the fuel gases before they are burned. The stack gas sulfur dioxide monitor will not be needed for refineries in any but very exceptional cases.

Specific methods for quantifying emissions have been mandated by the EPA for stationary source testing in order to demonstrate compliance with all performance standards. These are the Compliance Test Methods, as distinguished from Emission Monitoring Methods. The former are primarily manual, wet chemical methods. The

# Typical sample systems: new source performance standards



## Advanced systems



STACK SAMPLING SYSTEM

government has not specified the methods to be used for emission monitoring, except for opacity. However, the direction of current developments indicates that common usage may settle on certain types of automatic physical-chemical and electrooptical instrumentation.

There are three basic approaches to source monitoring that could foreseeably meet the current requirements of the EPA:

- extracting a continuous sample from the stack or duct and feeding it to any appropriate analytical instrument, after initial conditioning by means of a sample handling/interface system
- observing and analyzing the stack gases in situ by means of an optical instrument whose light path traverses the gases inside the stack or duct
- observing and analyzing the stack gases shortly after they leave the stack by means of remote optical instrument.

Commercial instrumentation, readily available for the first two approaches but not the third approach, has already been installed in a number of plants.

### Extractive vs. in situ

In the extractive approach, a continuous sample is drawn from the stack, or process stream, and transported to the analyzer, which can be mounted in any convenient location. A probe is mounted in the stack or duct, and some form of interface system provides the analyzer with a sample that is in an appropriate state of cleanliness, temperature, pressure, and moisture content. This approach is the oldest and has provided the most experience to date.

With the in situ approach, the instrument is mounted inside or just outside the stack. In the case of photometric and spectroscopic instruments, the light source may be mounted on one side of the stack and the detector on the other, so that the instrument scans the full width of the stack. Alternately, the instrument may incorporate an extended mechanical beam with a mirror on the end or a mirror may be mounted on the opposite side of the stack so that the light penetrates a fixed distance and is returned to the instrument on the same side. Since these spectroscopic instruments determine pollutant concentrations by their discrete spectral absorption, they must be capable of discriminating against absorption and scattering of the light by particles. They must also have high discrimination against all other unwanted components that are present in the stack gas, such as water vapor or carbon dioxide.

The in situ approach provides an average reading across the whole stack. This average is an advantage over the point sampling approach that is most common with the extractive systems. It is possible, however, to provide the averaging function with the extractive system by using multiple integrating probes. One problem facing all in situ optical instruments is that of keeping the optical windows clean. The common solution is to bathe the windows with a stream of clean air. This method appears to be fairly effective for a reasonable period of time, but periodic mechanical cleaning is required. Another problem with the in situ instruments is to provide a satisfactory method of checking zero and span periodically. Normally achieved with most analytical instruments by supplying known blends of zero and span gases to the instrument, this method is more practical with extractive systems.

In the case of extractive systems, there is often some question as to whether the sample interface system may absorb, or in some way modify the component of interest, particularly if it is chemically active. Such problems are at least partially overcome by the calibration procedure mentioned earlier since the zero and span gases can be introduced at the front end of the system, where they receive the same treatment as the sample. In situ monitors avoid all of the problems of sampling/interface systems that have been numerous and serious in the past. It is hoped newer developments in sample handling systems will overcome many of these problems. The extractive instruments are flexible in more ways than the in situ type. Some of the advantages of the extractive type instruments are:

- mounts in any convenient location, protected from the elements
- offers no limitation on stack, duct or process line size, temperature, or location, and can receive sample from any convenient and appropriate site
- provides dry basis analyses directly, with appropriate sample interface systems
- eliminates contaminating dust, dirt, and other interfering compounds through sample interface systems

- provides samples for multiple instruments with a single interface system
- monitors several stacks or process streams sequentially with one instrument.

In situ monitors require no sample interface system other than an air shield to protect the optics from solid or liquid contaminants carried by the stack gas. On the other hand, extractive-type instruments require a sample interface system to remove the sample from the stack or process stream and deliver it to the instrument in the proper state. Instruments differ in their sample requirements but, in general, the sample interface system must perform several or all of the following functions, depending on the nature and condition of the original sample: remove a representative sample from the stack or process stream; cool the sample, if excessively hot, and reduce its dew point; remove particulates; remove any condensate; raise the pressure of the sample, if subatmospheric, and/or regulate it at a constant pressure somewhat above atmospheric for delivery to the instrument; withstand corrosion by the sample constituents and not react with the component of interest in such a way as to change its concentration.

### Sample conditioning hardware

Appropriate hardware must be found or fabricated to perform the various functions indicated above. Sample acquisition is usually performed by a probe, attached to a pipe coupling which is welded to a hole in the wall of the stack, flue, or pipe. The probe extends an appropriate distance into the sample duct. It may be a simple pipe or it may have a coarse (5–30-μ pore size) filter attached at the end, fabricated of sintered metal, refractory, metallic screen, or fabric. Ordinary steel pipe is limited to a stack temperature below 1400°F (760°C) while 316 SS is usable to 16,000°F (870°C). At temperatures above this, a water-cooled steel probe may be used, or sillimanite (aluminum silicate) tubing, if the length is not over three feet. This material withstands temperatures up to 2800°F (1540°C), but has limited mechanical strength.

The sample conditioning system may be located directly at the sampling point, or it may be located some distance away, for convenience in installation and maintenance. In the latter case, a suitable sample line must be provided. Due to the reactive nature of several components normally found in combustion gases and sulfuric or nitric acid plant stacks, this sample line should be stainless steel or high temperature fluorocarbon and should be at least ⅜–½ in. inside diameter to avoid plugging. It is always mounted with a downward slope, and condensate pockets are carefully avoided. It may be heated to avoid condensate. This is particularly advantageous if the sample contains sulfur trioxide; the acid dew point for a concentration of 15 ppm being about 250°F (120°C). Steam, or electrical tracing is used for heating; steam being easier to control and providing a more uniform temperature, but electrical heating being more popular. Integral heated lines of either stainless steel or Teflon are available.

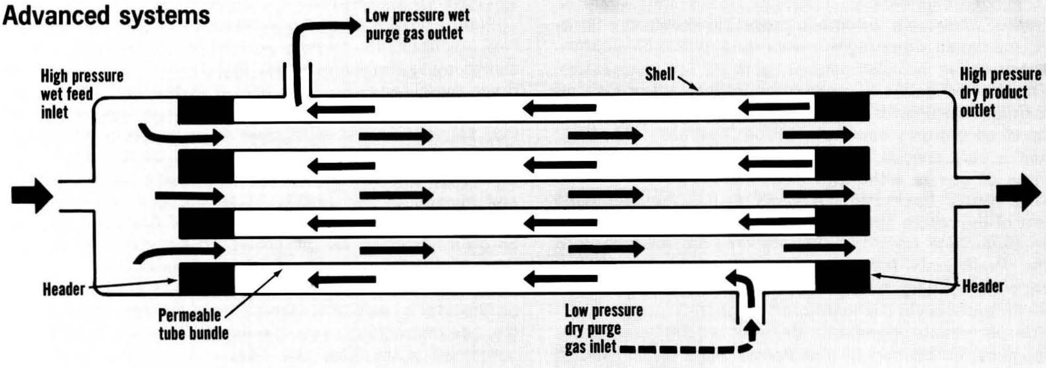
Sample cooling is simply for gases which have relatively low thermal capacity. A few inches of stainless steel sample line or a couple of feet of fluorocarbon line normally provide adequate cooling to protect an analyzer. Streams with dew points above the operating temperature of the instrument are normally cooled well below that temperature, however, to avoid any possible condensation within the analyzer itself. This may be accomplished with an air-cooled heat exchanger or with forced cooling, as with a refrigerated condenser or a Ranque Hilsch vortex tube.

Particulate removal can be achieved by many types of filter bodies and filter elements, utilizing different forms of both organic and inorganic material. Selection is based on the particle size and stream-loading factors, as well as the nature of the gases. Stainless steel is most commonly used for body material for stack gas filters and the filter element is selected for pore size and filtration area to remove even the submicron particles while not requiring too frequent maintenance.

Condensate removal after the heat exchanger can be effected by various types of traps. Corrosion resistance is obtained with stainless steel or other metallic alloys, or plastic. A good design provides minimum contact between the ongoing sample and the liquid condensate, and minimizes the likelihood of droplet carry-over by means of baffles or partitioning. Traps are available with either manual or automatic drain valves. The latter are more *expensive and complex, but require less attention*

Pressure control/adjustment, in the case of process streams where sufficient pressure usually exists to move the sample through the interface system and the analyzer, is by regulators of appropriate materials of construction or by relief valve on a side branch. In the case of stacks, flues, and vents, the pressure may be anywhere from 50 in. of water above atmospheric to 50 in. below. In this case some sort of mechanical pump must be used ahead of the regulator. Until recent years, appropriate pumps have not been plentiful and even now much needed development is under way in this area. Rotating carbon vane pumps have seen considerable use in the past, but bellows and diaphragm pumps with inert, internal coatings are coming into greater popularity now, particularly as more resistant and longer wearing components are being developed.

## Advanced systems



PERMEABLE MEMBRANE DRYER

## Monitoring requirements: new source performance standards

| Category I plants[a] | Monitor | Basic approach | Instruments |
|---|---|---|---|
| I. STEAM GENERATOR | | | |
| **A. Burning solid, liquid or gaseous fuel** | Nitrogen oxides | In situ | Spectroscopic |
| | | Extractive | Spectroscopic |
| | | | Chemiluminescent |
| | | | Polarographic |
| **B. Burning solid or liquid fuel** | Smoke opacity | In situ | Photometric |
| | Sulfur dioxide | In situ | Spectroscopic |
| | | Extractive | Spectroscopic |
| | | | Flame photometric |
| | | | Polarographic |
| II. NITRIC ACID PLANT | Nitrogen oxides | In situ | Spectroscopic |
| | | Extractive | Spectroscopic |
| | | | Chemiluminescent |
| | | | Polarographic |
| III. SULFURIC ACID PLANT | Sulfur dioxide | In situ | Spectroscopic |
| | | Extractive | Spectroscopic |
| | | | Flame photometric |
| | | | Polarographic |
| **Category II plants[b]** | | | |
| I. PETROLEUM REFINERY | | | |
| **A. Fluid cat cracker catalyst regenerator** | | | |
| **1. All** | Particulate opacity | In situ | Photometric |
| **2. Regenerators without waste heat boilers** | Carbon monoxide | Extractive | Spectroscopic |
| **3. Regenerators with waste heat boilers** | Stack gas oxygen | Extractive | Polarographic |
| **B. Process heaters, boilers and waste gas disposal systems** | | | |
| **1. Firing higher level $H_2S$ (with $H_2S$ removal)** | Stack gas $SO_2$ | In situ | Spectroscopic |
| | | Extractive | Spectroscopic |
| | | | Flame photometric |
| | | | Polarographic |
| **2. Firing gas containing less than 230 mg/$Nm^3$ $H_2S$** | Fuel gas $H_2S$ content | Extractive | Chromatographic |
| II. IRON AND STEEL PLANTS | | | |
| **A. Basic oxygen furnace[c]** | Particulate opacity | In situ | Photometric |

[a] Promulgated by EPA December 1971. [b] Promulgated by EPA March 1974. [c] Requirements forthcoming.

### Newer developments

Several new pieces of sample-conditioning hardware have appeared on the market within the past year or two. They represent both improvements on existing equipment and the application of entirely new techniques. One such stack gas interface system was designed to utilize several of these recent developments. It was successfully tested during the last quarter of 1973 on a coal-burning power plant stack. Eventually, it is hoped, the system can be markedly simplified and its overall size decreased proportionally. While it was originally designed specifically for the coal-fired combustion stack, it should also be applicable to other types of stationary sources, possibly with minor modifications. Presently, the system features a "reflux" probe, an automatic probe blowback, dry filtration, multihead diaphragm pump, and permeable membrane drying.

The "reflux" probe is a new proprietary development of Beckman Instruments, Inc. Externally it has the appearance of an ordinary open tube probe. Internally, however, it has a very special configuration. In operation, a large volume of gas is withdrawn from the stack and a large part is forced back into the stack at high velocity. The effect of the return stream is to shield the end of the tube from particulate material, allowing only the gas phase to enter. Preliminary tests indicate that the probe reduces particulate loading in the sample by better than 98%, even for particles in the submicron range.

The permeable membrane dryer is another recent development, introduced by the Perma Pure Products Co., Inc. (Oceanport, N.J.). As described by its inventor, the dryer uses a permeable membrane as a desiccant, and a dry gas for continuous regeneration. The dryer is designed as a tube-in-a-shell configuration where the sample may enter one side of the membrane and the dry purge gas flows on the other side. Its advantage is that the sample is dried with no loss of $SO_2$, NO, or $NO_2$.

Basically, a rather large volume of sample is removed from the stack through the reflux probe, as described earlier. Most of this is drawn through an aerosol removal /filtration stage and returned to the stack, by one head of the diaphragm pump, to provide the particulate barrier. A smaller portion of the sample, taken beyond the aerosol removal stage, is drawn through another filter and forced, under pressure, into the membrane dryer, by a second head on the pump. After leaving the dryer, this sample is available for the analyzer or analyzers.

Plant air, with oil and condensate removed, is used for two functions. Its primary service is as a carrier gas to sweep away the water vapor that passes out through the dryer membrane. For this use, it is first put through an automatic heatless dryer. The dried air is then expanded into the shell of the membrane dryer which is maintained at reduced pressure by a third head of the diaphragm pump. By pressurizing the sample inside the membrane and expanding the carrier air on the outside, maximum drying is achieved. The second use of the plant air may be as a blowback for the probe. To achieve this, the ball valve is opened automatically for 1 min each hour.

The complete system is mounted in a cubicle, directly on the stack, with the probe extending from the back of the box immediately into the stack. The components are contained in an inner box heated to prevent condensation. The multihead pump is outside of the heated box, but with very short insulated lines leading into the heated area. Calibration gases can be introduced ahead of the sample filtration/drying stage so that they receive exactly the same treatment as the sample itself. Alternately, they may be introduced at the analyzer inlet to check the effect of the interface system on their concentration.

Several features of the system are still somewhat experimental and it is expected that considerable simplification will be possible. For example, a portion of the dried sample itself may serve as carrier for the permeated moisture. Thus, the need for plant air can be eliminated. With such simplifications and resulting size reduction, the complete system may eventually require no more than 1 or 2 ft$^3$ of volume and will become literally portable.

## Performance standardization

At present, the performance of stationary sources, in respect to compliance with the established emission standards, is determined by the manual testing procedures stipulated by the EPA. These methods were selected, in so far as possible, from standard methods, long established and widely used in industry, and of more or less proved validity. Few, if any, instrumental methods fit these criteria, primarily because industry has not made use of them in the past, due to their expense and the lack of any motivation to use them. Now that certain instrumental monitoring requirements have been established by the Government, experience with such systems will grow. As soon as the validity of the instrumental systems is established, they will undoubtedly become standard accepted methods, and will probably supplant the manual procedures in many cases. The current problem remains to provide a method whereby instrumental systems can be validated.

As long as the manual methods remain the legally accepted standards, instrumental systems must provide the same results as the reference methods to be legally valid. This situation is what has given rise to the concept of equivalency. Any new candidate method must be demonstrated to be equivalent to the standard reference method to be certified as valid. As yet, no procedure has been established for the demonstration of equivalency.

That is because the standard methods themselves are generally not nearly so precise as instrumental methods, and quite possibly not so accurate. Also, the standard methods generally give results that are averages over an appreciable period of time while the instrumental methods give results approaching real-time data, thus rendering direct comparison of results questionable. Analytical results may be affected markedly by sampling procedures and it is not possible to provide identical sampling procedures for both candidate and standard methods.

The accumulation of statistically meaningful quantities of comparative data is difficult due to the cumbersome nature of the standard methods. For comparative data to be meaningful with reference to stack measurements, the testing must be performed in the field on actual installations of complete systems. The sample interface must be treated as part of the complete analytical system and the complete system tested as such. Furthermore, the present judgment of the EPA is that each and every individual analytical system should be validated after installation. This adds at least $8000 to the cost of the installed system. At the present state-of-the-art, this is a valid judgment, but it raises the question of how costs should be divided between manufacturer and purchaser, particularly in the event that the system should not pass the tests in a particular installation. We hope future developments and experience will alleviate some of these problems.

Several attempts have been made to evaluate monitoring instruments through EPA contracts. None of these, which have been published to date, have produced the type of data that would allow official certification of any specific instrument systems. This is partly due to the rapid development in new instrumentation, and partly due to unsuccessful or unrepresentative sample interface systems. Several other evaluations have been performed both within the federal agency and by private organizations but, again, either the results were not published or they were inconclusive.

At the end of 1971, Beckman Instruments performed field testing on an analytical system incorporating the NDIR sulfur dioxide analyzer and the NDIR nitric oxide analyzer, installed on a coal-fired power plant stack. Although the test was thorough and the results conclusive to both the instrument company and the customer, the evaluation did not result in any certification by the EPA and was, therefore, of limited and short-term value.

At least part of the problem could be solved if there were standard methods for testing the performance of the analytical instruments and expressing the results. Work is under way toward this end within the International Electrotechnical Commission (Geneva, Switzerland). Working Group 6 within IEC Technical Committee 66 has prepared a recommendation for "Expression of the functional performance or nondispersive infrared analyzers used for the continuous determination of air quality." It applies to nondispersive infrared analyzers used for measuring pollutants, either in the ambient air or in gaseous streams entering the ambient air. It includes definitions of terms, test procedures, and forms for expressing certain performance parameters that it requires the manufacturer to state. This draft was circulated to the full Technical Committee as document 66 (Secretariat) 19 dated May, 1973, and was discussed in the plenary meeting of the Committee in The Hague on October 29–30, 1973. It was approved, with minor changes, and submitted to the "six month rule." After editing, it will be presented for final comment to the national committees around the world. The second document, on water quality instruments, pH, electrical conductivity, dissolved oxygen, and ORP, is now in preparation.

## Additional reading

"Proposed Performance Specifications for Stationary Source Monitoring Systems for Sulfur Dioxide and Nitrogen Oxides and Visible Opacity," unpublished draft, January 1972, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

"Background Information for Proposed New Source Performance Standards," Vol. 1, June 1973, U.S. Environmental Protection Agency, Research Triangle Park, N.C. (See also *ES&T,* October 1972, p. 884.)

"Continuous Monitoring of Stack Gases," K. Rosenthal and R. J. Bambeck, ISA Proceeding, 1972, *Anal. Instrum.,* **10**, ISA, Pittsburgh, Pa.

*Instrumentation for Environmental Monitoring,* Vol. 1, May, 1972, Environmental Group, Lawrence Berkeley Laboratory, University of California, Berkeley, Calif.

"Qualification Testing of an Infrared Analyzer System for $SO_2$ and NO in Power Plant Stack Gas," R. D. Jaquot and E. A. Houser, ISA Proceedings, 1972, *27th National Conference and Exhibit,* Part 3, 730, ISA, Pittsburgh, Pa.

**Robert L. Chapman** *is with the process instrument division of the application engineering department at Beckman Instruments, Inc. He has published a number of papers on process and environmental analysis instrumentation.*

*Coordinated by LCG*

# INDUSTRY TRENDS

**Koppers Co., Inc.** began operation of a new boiler system that incinerates waste gas to produce plant process steam and heat where coal was formerly used. The plant makes maleic anhydride; the system surpasses legal environmental requirements.

**Calgon Corp.** has completed a $106,000 wastewater survey and analytical program at three power stations of the Tampa Electric Co. (Fla.).

**Ecodyne Corp.** will construct four concrete mechanical draft-cooling towers for two 720-MW fossil-fueled power plants for Carolina Power & Light Co. near Roxboro, N.C.

**Beckman Instruments, Inc.** will supply exhaust analysis systems to Ford Motor Co. for $400,000 for use in new engine research and development programs.

The firm of **Hailstone Associates** was formed in Dallas, Tex., to offer technological consulting services, including environmental control, to the minerals processing industry.

**The Fourth Sink Management Group, Inc.**, was organized at Kattskill Bay, N.Y., to foster recovery and reuse of resources from solid wastes.

**General Atomic Co.** (San Diego, Calif.) is expanding its reverse osmosis system for Texas Instruments' semiconductor operation to produce over 1,045,000 gpd of ultrapure water. The system will be the largest of its kind in the world.

**American Air Filter Co., Inc.** received a letter of intent on an $8.6 million order for environmental control equipment for the 1860 MW Almaraz Nuclear Power Station (Spain).

**Burns and Roe, Inc.** was awarded a $205,741 contract for a preliminary engineering report on a 100-million-gpd desalting project in the lower Colorado River Basin.

**Research-Cottrell, Inc.** will build three electrostatic precipitators for Indiana & Michigan Electric Co. of the American Electric Power System. The cost is over $7 million.

**Westinghouse Electric Corp.** received an order for 12 nuclear steam supply systens, each 900 MW, from Electricité de France. Cost is $200 million each.

**Cambridge Filter Corp.** has acquired Root Engineering Corp. (Whitehouse, N.J.), a designer of pollution control systems. Terms were not disclosed.

**Ionics, Inc.**, a manufacturer of air and water pollution abatement equipment and instruments, announced a net income of $571,000 for 1973. This amounts to $0.66/share, as compared to $0.49/share in 1972.

**Poly Con Corp.** will design and fabricate an ammonium recovery and fluorine abatement system, under contract to Badger Co., Inc. (Raytheon), for Occidental Chemical Co. at White Springs, Fla.

**Koppers Co., Inc.** has reorganized its Environmental Systems Division into Environmental Elements Corp., whose facility will remain in Baltimore, Md.

*(continued on page 528)*

# TRACE METALS IN AIR

## A new technique

Traditionally, the only method available for measuring the trace metal concentration in air has been to draw air through a filter for a long time (say, 8 or 24 hours) and then to identify the particles trapped on the filter by analysis. This procedure gives an average metal concentration but cannot give a measure of *variations* during the sampling period. To measure the variations, we need to analyze small samples of air, drawn through a filter for a very short time.

A new technique has now been developed by Varian Techtron for the specific purpose of collecting and measuring these small samples.

The Varian Techtron Air Microsampler is a new, highly sensitive air particulate sampling method which supplements the existing large-volume methods. For the first time, simple and effective tracking of the variations in trace metallic elements in air is possible.

In practice, a disk of filter material is placed in a small graphite cup with a perforated base, and air is drawn through the filter with a simple pump. Collection time is about two minutes. The cup with its sample is then transferred to the Varian Techtron Carbon Rod Atomizer for analysis.

In the Carbon Rod Atomizer, the cup is heated electrically through three programmed stages: drying, ashing and then atomization. In the atomization stage the pollutant concentration is measured by atomic absorption.

The Air Microsampler makes the most of the excellent analytical sensitivity of the Carbon Rod Atomizer by allowing very low concentrations of metals in air to be quantified. The sensitivity for lead analysis in a 200 ml air sample is 0.1 $\mu$g/m$^3$, and for cadmium the sensitivity is 0.008 $\mu$g/m$^3$.*

In principle, the Air Microsampler could be applied to any metal of interest, and in any atmosphere. In each situation the new method will give a measurement of the airborne metal concentration at a point in time, and by consecutive sampling the variations can be followed over an extended period.

Further details are available from Varian offices.

***Matoušek J. P., Brodie K. G.,**
Direct Determination of Lead Airborne Particulates by Non-Flame Atomic Absorption, Anal. Chem., 45, (9), 1606, 1973.

**Brodie K. G., Matoušek J. P.,**
Determination of Cadmium in Air by Non-Flame Atomic Absorption Spectrometry, Anal. Chim. Acta., 69, (1), 200, 1974.

varian

**Varian Techtron**
Palo Alto, Cal., U.S.A.
Georgetown, Ont., Canada
Zug, Switzerland
Springvale, Vic., Australia

CIRCLE 12 ON READER SERVICE CARD

**Environmental Data Corp.** announced receipt of five contracts from five U.S. companies, exceeding $200,000, for $NO_2$, $SO_2$, $CO_2$, CO, and opacity monitoring instruments.

**Dames & Moore** (Los Angeles, Calif.) will prepare environmental reports for three candidate sites for a San Diego Gas & Electric Co. fossil-fueled power plant.

**Climatronics Corp.,** a manufacturer of meteorological instruments and systems, has expanded its office and manufacturing space fivefold at Hauppauge, N.Y.

**Engelhard Kali-Chemie AutoCat GmbH** (Hannover, Germany) will supply Engelhard "PTX" automotive catalysts to the makers of Mercedes-Benz, Peugeot, and Renault cars.

**Wheelabrator-Frye** received a more than $75 million order from Detroit Edison Co. for air pollution control systems.

**Scott Paper Co.** (Philadelphia, Pa.) spent $22 million for environmental control (ec) in 1973. Another $85–130 million will be spent for ec through 1978.

**Neville Chemical Co.** (Pittsburgh, Pa.) started up its $750,000, 50,000-gpd final treatment system to reduce phenol to 0.1 ppm in its Neville Island, Pa., plant effluent.

**SWECO, Inc.** and **Equipos de Proceso, S.A.** (Mexico) formed SWEQUIPOS, S.A., at Tlalnepantla, Mexico, to make and market SWECO screening equipment in Mexico.

**Texaco, Inc.** gave a construction contract for a 3.8-million-gpd wastewater treatment plant for its Port Arthur, Tex., refinery to Williams Brothers Waste Control, Inc.

**MacMillan Bloedel, Ltd.** (Canada) has acquired control of Energex, Ltd. (San Diego, Calif.), which developed a pollution-free cyclonic burner that converts waste material into energy.

**Pollution Control-Walther, Inc.** has booked about $39 million in contracts for 68 Walther electrostatic precipitators over an 18-month period ended March 31, 1974.

**Pure Aire Corp.,** an Envirodyne company, was selected as one of the outstanding Pacific Coastal Region small business manufacturers by the U.S. Small Business Administration.

**Combustion Equipment Associates, Inc.** will build a combination waste-to-energy and pollution control facility for Synthane-Taylor Corp. at Valley Forge, Pa.

**Biospherics, Inc.** has received orders for 55 Cleansimatic Liquid Analysis Meters (CLAM) for municipal sewage monitoring at Annapolis, Md., and Contra Costa County, Calif.

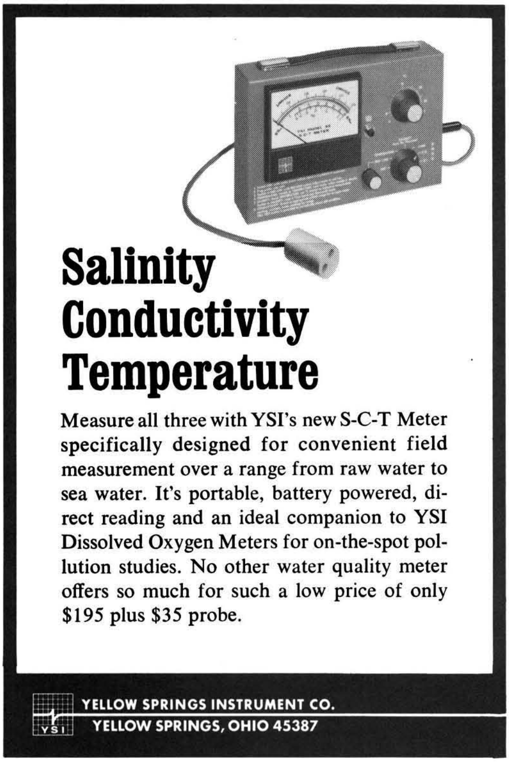
**Combustion Engineering, Inc.** will supply two 865-MW "Combined Circulation" steam generating units to Georgia Power Co. for $44 million.

**NRG Inc.** (Phoenix, Ariz.) formed a new subsidiary, NRG NuFuel Co., to work with natural gas, and especially with methane recovery from sanitary landfills.

**Frost & Sullivan, Inc.** (New York, N.Y.) predicts $10 billion federal spending on energy research and development over fiscal years 1975–79, in a 286-page analysis.

**Gorham International, Inc.** (Gorham, Me.) is studying possibilities for profitable approaches to managing the pulp and paper industry's increasing wastewater sludge quantities. A number of clients are involved.

**Jeffrey Manufacturing Co.** has licensed NGK Insulators, Ltd. (Nagoya, Japan) to manufacture and sell Jeffrey's line of sewage treatment equipment in Japan.



John McStravick and the President of Energetics Science, Inc., H.C. Lieb, weren't surprised by reader response to the Ecolyzer.

Remember all
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Heat/Line Hose is built to the same high standards as the most sophisticated gas analysis equipment.

Since all components are bonded into one integral unit, the hose is extremely pliable and flexible. Moreover, it resists kinking. (For example, our ⅜″ I.D. model has a 4-inch bend radius!)

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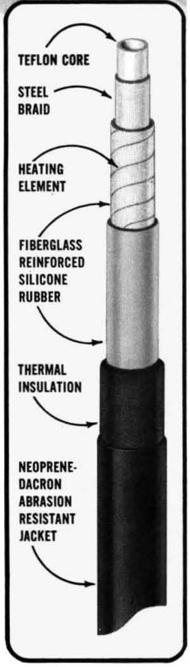

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# NEW PRODUCTS

**Air sampler**
Equipped with nickel cadmium, self-charging batteries, air sampler can be used with equal efficiency both indoors and in the field. The device is portable, weighing only 8 lb. Manufacturer states the unit will withstand the most severe environmental operating conditions. It will sample air for all types of airborne particulates and pollutants. Staplex Company, Inc. **101**

**Flow recorder**
Open channel flow recorder measures in either English or metric units, and can be used with any type and size of weir or flume. Easy field change of cam and gears permits instrument to record from a range of 14,000 gpd through a 22.5°-V-notch weir up to several hundred million gpd through large flumes. Accessory: a sampler switch for actuating a remote sewage sampler to flow. Leupold & Stevens, Inc. **102**

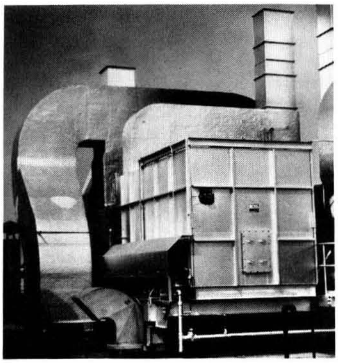
**Metal recovery system**
System economically recovers precious metals from plating rinse waters. This "closed loop" system can be used on all types of precious metal plating including gold, silver, rhodium, platinum, and palladium. The device reduces water consumption by returning decontaminated and deionized rinse water to the rinse tank for reuse. Mixed-bed ion exchange column, which contains special resins, is utilized. Reuter-Stokes, Inc. **103**

**Urban tree feeder**
Indestructible underground tree feeder is designed to help preserve the beauty and benefits of urban trees. This water, air, nutrition exchange system protects and revitalizes tree roots suffocating under layers of paving materials. The individual units in the system are placed underground around the tree in line with the outer reaches of the leaf canopy. W. A. N. E. Tree Systems. **104**

**Stack sampler**
Isokinetic stack-sampling system meets EPA requirements. System includes all instrumentation, glassware, and other equipment needed for measurement and control of sampling parameters. It maximizes serviceability and ease-of-handling in either horizontal or vertical sampling, or particulate and condensable emissions. Arthur H. Thomas Co. **105**

**Pump controller**
Electronic method controls speed of ac-wound rotor motors while recovering and regenerating static power. System is designed for use with water and waste pumping systems utilizing 25-hp motors and larger. Can capture and regenerate 97% of the electrical power conventional control systems waste for an overall savings of 10 to 40%. Marathon Electric. **107**

**Bioassay test kit**
Kit utilizes microorganisms to provide quick indication of the presence of bioinhibitory agents that may be present in wastewater. Results normally are obtained in 2 hr or less compared to 96 hr for standard fish bioassay. Toxic or inhibitory contaminants are detected by a colorimetric assay of growth activity of a specialized nonpathogenic seed. Chemical-Industrial Labs Inc. **108**



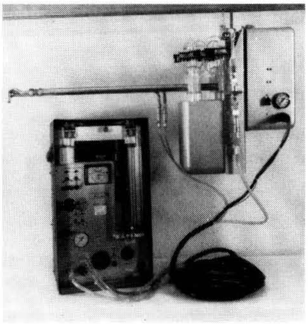
**Fume incinerator**
Thermal fume incinerator will recover up to 100% of the BTUs required to incinerate the solvent fume load. Heat recovered can be used for preheating combustion air, drying or other process applications, space heating, or makeup air in wide range of industries, and for sewage and waste treatment. Incineration is completely effective on a wide range of combustible organic fumes and particulates. Ross Engineering. **106**

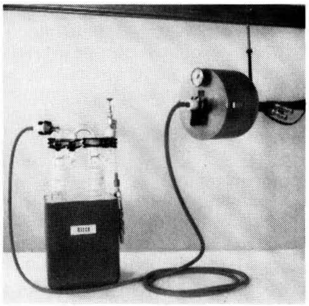
**Chloride analyzer**
Salt analyzer provides accurate, immediate, easily read measurement of chloride content. Device requires only limited use of chemicals, has an easily read digital readout, and can be used by unskilled personnel. It will detect most inorganic chloride ions in a constant background, making it useful for most applications where chloride content control is important. Diamond Crystal Salt Co. **109**

**Recycling process**
System processes virtually all types of waste paper materials and does not require the use of water. It thus is almost totally nonpollutive to the environment as a closed system with no discharges. Manufacturer claims it lends itself particularly to the establishment of recycling and reclamation centers in urban areas because of the relatively low cost of the physical plant required. Simplex Industries, Inc. **110**

**Submersible pump**
Large electric submersible wastewater pump is designed especially for high head applications up to 140 ft. It features a three-channel nonclog impeller and a 170-hp motor. Discharge size is 12 in. and pump capacity can range to 6200 gpm. The pump can be raised along special guide rails for inspection or maintenance without need for personnel to enter the well. It is suitable for either wet or dry pit installation. Flygt Corp. **111**

**Particle screener**
Custom designed stainless steel spark and particle arrestor is designed for commercial, industrial, and residential applications. Made of $\frac{3}{4} \times \frac{3}{4}$-in. mesh wire, the arrestor screen has exceptional resistance to heat and corrosion and retains smoke stack particles combustion sparks. Firm will fabricate screen to size or provide wire cloth in full rolls. Newark Wire Cloth Co. **112**





**Water monitor**

All-electronic monitor accurately measures rate of water flow on a 30-day chart recorder without floats, probes, mechanical linkage, or bubblers. It uses an imbedded sensor-element in a formula measuring flume to generate data for the control cabinet's electronic logic circuits. It performs this by relating water depth to flow rate. Universal Engineered Systems, Inc. **113**

**Cyanide test kit**

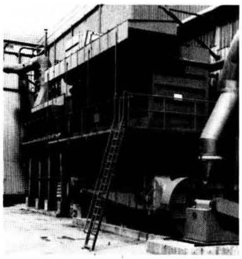
Interference-free cyanide spot test kit identifies traces of free and bound cyanide. It is intended for use with wastewater, food, soil, and biological samples. Based on fluorescent reaction, as little as 0.1 ppm bound cyanide may be detected in matter of minutes. Contains necessary materials and reagents for 100 tests. Ultraviolet lamp available as option. Koslow Scientific **114**

**Centrifugal thickener**

Single centrifugal thickener mechanically dewaters liquid concentrates in wastewater processing. In many cases it eliminates the need for thickening tanks, centrifuges and vacuum filters. Municipal applications include thickening of primary and waste activated sludges. It can remove all materials larger than 25 $\mu$ and discharge them as sludge of up to 50,000 ppm. SWECO, Inc. **115**

**DO/BOD/temperature analyzer**

Multiple-range analyzer covers all needs for dissolved oxygen, BOD, and temperature tests in every type of municipal and industrial treatment plant. Rugged portability and gasketed, splashproof construction also make it suitable for stream and pollution studies outside the plant. Instant air calibration makes it easy to use. Delta Scientific **116**

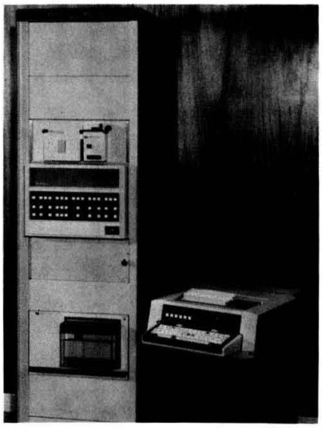


**Fabric filter system**

System provides a pre-engineered approach to particulate and fume emission control. Unique air-to-air heat exchanger is part of the system's solutions to the processing of high-temperature exhaust gases. Advanced envelope-type design, combined with gentle pulsating reverse-air cleaning and provisions for effective gas precooling, provides operational benefits. Lear Siegler, Inc. **117**

**Waste compactor**

Stationary waste compactor can be operated from both on-site and remote control stations. This 2-yd$^3$ capacity unit is designed for cost-cutting, efficient waste compaction applications from heavy industry, supermarkets, schools, and universities to hotels, restaurants, apartments, and shopping centers. Featuring a 45-sec cycle time, it has a volume displacement rate of 121 cyph. Gar Wood **118**



**Data analysis system**

Computer-based system for pollution data acquisition and analysis allows for continuous, unattended data acquisition 24 hr a day from numerous remote terminals. System is particularly suited to testings covering a wide area from one central point because remote terminals interface directly to existing instruments or sensors. DRT Associates **121**

**Wastewater separator**

Water-oil-solids separator features oil flotation, effected by the upward flow gradients, while solids settle out from the action of downward gradients. Two cone screens located in the center of the tank prevent jetting by diffusion. Clarified water is removed at one top port and oil from another. Sludge is removed from the bottom. Industrial Process Systems, Inc. **119**

**Odor measurer**

Instrument is capable of determining the concentration of a malodorant in ambient air or in a captured gas sample from an emission source. It utilizes the olfactory receptors of the human nose. Observers require very little training to produce accurate and repeatable measurement of odor concentrations. Can be operated in laboratory, from vehicle, or in field. MISCO **120**

**SO$_2$/opacity monitor**

Monitor allows power plant operators to mix fuels of different sulfur content for optimum economy while remaining within prescribed emission levels. Instruments are mounted directly on the stacks and employ polychromatic light passing through the flue gas as the means of analysis. Monitors do not require expensive sample lines, filters, or reagents. Response time less than 4 sec. Environmental Data Corp. **123**

**Submersible pump line**
Designed for heavy duty sewage uses, submersible pump line is capable of handling solids up to 2½ in. in diameter through its 3-in. discharge. It has pumping capacity of 22,200 gph and heads up to 43 ft. Pumps are suitable for use on barges, in dual filter beds, lift stations, rotary arm aerators, utility tunnels, grain elevators, and for dewatering mines, tunnels, and construction projects. Kenco Pump Division **124**

**Ozone meters**
Series of ozone meters utilize the photometric detection of the chemiluminescence resulting from the flameless reaction of ethylene gas with ozone. Other oxidizing and reducing species normally found in ambient air do not interfere. Five models are offered with ranges of 0–5.0 ppm, 0–50 ppm, 0–500 ppm, 0–5000 ppm, and 0–10,000. McMillan Electronics Corp. **125**

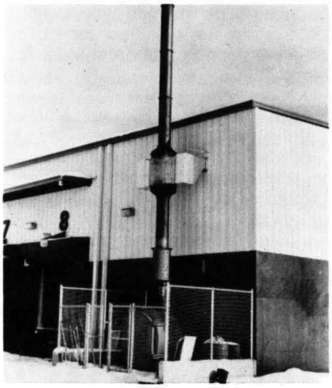
**Pedestal-type Aquamast**
Fully automatic spraying device is designed for land disposal of waste effluent. It can be furnished for capacities to 8000 gph to cover up to two acres. The unit can be transported from place to place, as required, by mobile crane. In operation, it rotates very slowly, spraying waste effluents uniformly on the ground through a series of sprinklers positioned along booms. McDowell Manufacturing Co. **126**

**$H_2S$ removal system**
Process converts $H_2S$ directly to high-purity elemental sulfur at a high removal efficiency. It operates at moderate temperatures, is not sensitive to gas pressure or high partial pressures of carbon dioxide, and does not produce a tail-gas problem. Gas to be purified is countercurrently scrubbed in an absorber containing a vanadium salt. Peabody Engineered Systems **127**

**Flocculation system**
System will greatly improve flocculation of suspended solids normally present in water treatment systems prior to removal by sedimentation of filtration. It consists of a solid bar of specially compounded polyelectrolyte enclosed in a sock of fabric selected to control emission of the flocculating agent. It can be used for emergencies or to improve flocculation efficiencies of conventional systems. Aqualogic Inc. **128**

**Water pollution analyzer**
Analyzer measures total organic carbon, total carbon, total oxygen demand, and handles a large sample, up to a liter, solids included. No filtering or homogenization is required. Sensitivities from trace to several per cent can be provided, measuring time varying with dilution from about 2 min at high concentrations. Easy to load. Astro Ecology **129**

**Shredding system**
With a capacity of 20 tons per hour, shredder will handle dunnage such as wooden palets, shipping cartons, and pieces of heavy material such as canvas. All such waste is shredded to reduce bulk and to simplify disposal. A metallic separator removes ferrous matals for resale. Several models are available. The Heil Co. **130**



**Energy recovery incinerators**
Packaged energy recovery systems have recovery rates from 300,000 Btu/hr to 2.7 million Btu/hr. They are available in three versions—air to air, air to water, and air to steam—for heating plants, offices, or for in-process use. Recovery is generated in a heat exchanger mounted in the incinerator stack. Heat is transferred by conventional ductwork, piping, or other means. Kelley Company, Inc. **131**

**Particle counter**
Portable analog particle counter continuously monitors airborne particulate matter 0.5 $\mu$ and larger in concentrations between 10,000 and 10,000,000 particles/ft$^3$. Audio alarm warns when preset particle concentration is reached. Lightweight, counter combines rugged shock mounted sensor with solid-state components for high accuracy. Climet Instruments **132**

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*Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.*

# NEW LITERATURE

**Publication list.** Catalog for 1974, giving new publications and educational aids, offers a list of books, conference proceedings, and educational aids covering instrumentation, sensing devices, uses, and safety practices. Environmental monitoring is included. Instrument Society of America. **159**

**Catalog.** 1974 catalog that company has prepared (32 pages) includes tubing pumps and drive systems, as well as newly introduced 5- and 10-channel pump drives. Also covered is laboratory equipment and a new bench-scale biooxidation system. Cole-Palmer Instrument Co. **160**

**Filters.** Bulletin TI-63 describes filters for sterile air, or gas filtrations, and their use. Sterile filter system design and operation are discussed. Balston, Inc. **161**

**$H_2S$ removal.** A 4-page brochure describes a proved method for converting hydrogen sulfide ($H_2S$) to elemental sulfur. A flow sheet is included. Peabody Engineered Systems **162**

**Gas scrubbing.** An 8-page, four-color bulletin (E-670) describes the company's system for fly ash, $SO_2$, and $NO_x$ compounds from coal, oil, and refuse-fired steam generator flue gases. Krebs Engineers **163**

**Management services.** A 4-page, illustrated publication describes the company's range of liquid waste management services for industry. Gilbert Associates, Inc. **164**

**Analysis technique.** Company's latest quarterly engineering issue (Vol. 7, No. 1) describes an easily accomplished multicolumn technique overcoming sticky problems of analyzing volatiles in a nonvolatile matrix by gas chromatography. Carle Instruments, Inc. **165**

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*Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.*

**Energy savings.** Brochure describes a new aluminum slider replacement window, NuPrime Model 565, designed to reduce heating and cooling for commercial establishment by up to 30%. Season-All Industries, Inc. **166**

**Calibration system.** Bulletin No. C-70 describes a permeation tube–calibration system for pollution monitoring and laboratory instruments. Mast Development Co. **167**

**Training programs.** Newsletter (Vol. 3, No. 1) tells how to save money by setting up low-cost training programs for laboratory technicians. Duke Standards Co. **168**

**Technology arguments.** First of a series of white papers intended to promote better understanding of the role of technology in society. Gould, Inc. **169**

**Atomic absorption.** New brochure No. AA 322E covering techniques and applications of atomic absorption spectroscopy, as well as a summary of atomic absorption reprinted articles is available. Perkin-Elmer **170**

**Noise reduction.** Case history bulletin No. 7428 describes use of a valence heating and cooling system to reduce ambient noise while maintaining controlled draft-free room temperatures in a nursing home. Edwards Engineering. **171**

**Filters.** Bulletin No. KL4206 covers advanced filtration technology in the form of mixed media filter materials. Neptune MicroFLOC Inc. **172**

**Settlers.** Bulletin LT-101 explains the principle and design of gravity settlers for removing precipitated metal hydroxides from metal finishing waste streams. Parkson Corp. **173**

**Buyers guide.** Bulletin 5391 lists systems for aeration and degasification, controls, instruments, clarifiers, filters, ion exchangers, and large industrial, municipal, and process wastewater treatment systems. Permutit **174**

**Metering pumps.** Brochure (Cat. file 400,000) lists types and general descriptions of metering pumps. Some pumps are usable for slurries or acid chemicals and inlude diaphragm pumps and plunger pumps. Wallace & Tiernan **175**

**Flexible linings.** Brochure WFL-73 describes linings of butyl rubber, neoprene, vinyl, and other flexible materials for many water pollution control purposes. Watersaver Co., Inc. **176**

**Filters.** Brochure 123B, 12/73 describes endless belt-type filters and their operation. Komline-Sanderson **177**

**Valves.** Brochure G-5B covers water level control, pressure control, surge control, and pump control valves. Uses are listed. Golden-Anderson Valve Specialty Co. **178**

**pH control.** Bulletin K-15B describes measurement and control instrumentation and systems and their applications. The Foxboro Co. **179**

**Biological system.** Brochure No. 373 describes a rotating biological surface system of wastewater treatment. Flow diagram and process advantage list are given. Environmental Pollution Control Division of Geo. A. Hormel & Co. **180**

**Technical report.** Company report on hydrogen peroxide and its uses in industrial waste treatment. Case histories, chemical equations, and graphs and charts are included. FMC Corp. **181**

**Test kits.** A 44-page catalog, General Catalog No. 74, lists a whole line of water quality and pollution control instruments and test kits. Order blanks are furnished. Ecologic Instrument Corp. **182**

**Screens.** Bulletin G-140 describes screens for removing solids from municipal and industrial wastewater systems, and reducing BOD with reduced operating costs. Combustion Engineering, Inc./Bauer **183**

**Anodes.** Company brochure describes anodes for corrosion protection, meeting military specifications. Dimensions and weights are given in

English and metric units. Sentinel Anode Co., Div. Peco Manufacturing Co., Inc. **184**

**Soil conditioner.** Company booklet about "Styromull" explains how to recycle foamed polystyrene coffee cups, packaging, and insulation to aid plant growth and help prevent plant disease, improve thermal balance in soil, and accelerate drainage. BASF Wyandotte Corp. **185**

**Air pollution technology.** New brochure No. 472 updates descriptions of engineering services, stack testing devices, and computerized duct collection system designs. Pollution Control Systems Division, Geo. A. Hormel Co. **186**

**Reverse osmosis.** Technical papers by company president, together with bulletins covering products, are offered in reverse osmosis and dialysis for electroplating and metal finishing wastewater. Osmonics, Inc. **187**

**Pump.** Bulletin CP-1 describes low-temperature centrifugal immersion pumps capable of circulating fluids from liquid nitrogen temperatures to 200°C. FTS Systems, Inc. **188**

**Technical report.** Brochure tells how a small town decided to rehabilitate sanitary sewers by sealing leaking joints internally. The technique was utilized for 5–10% of the cost of building two waste stabilization ponds. National Power Rodding Corp. **189**

**Feeder systems.** Brochure describes chemical solution and slurry feeders in company "flyer" sheet, along with flowmeters. Specifications are given. Ecodyne Corp. **190**

**Loading mechanisms.** Brochure SWH-72483 announces a new group of high-tonnage loading mechanisms for scrap metal handling, wrecking, and salvage materials. The Heil Co. **191**

**Laboratory products.** Catalog 74 lists over 40,000 products for the laboratory, and has 1275 pages of information arranged in convenient product-related groups. Fisher Scientific Co. **192**

**Oil skimmer.** A catalog, which includes the latest specifications and capacities of the company's oil skimmer, is available. Operational descriptions are given. Aerodyne Development Corp. **193**

**Clean energy.** Publication, "Air Journal," 16 pages, Winter 1974, describes efficient combustion methods, heat recovery, and production of clean-burning fuels. Other related articles are included. Peabody Engineering Corp. **194**

**Booklet.** Environmental testing booklet, written for the engineer who operates temperature, humidity, or altitude chambers, is available. Tenney Engineering, Inc. **195**

**Catalog.** Catalog AIC-2000, "Reflections on Pure Water Storage," covers ultrapure water storage tanks for hospital, electronics, pharmaceutical, cosmetics, food processing, or industrial applications. American Sterilizer Co. **196**

**Calculator program.** Booklet entitled "HVAC design with the HP 9810" describes ready-to-use calculator programs for heat loss–heat gain, building peak solar heat gain, duct sizing, and water and gas pipe sizing. Hewlett-Packard. **197**

**Flameless atomizer.** Illustrated booklet covers sampler for heavy metals in water in concentrations as low as 0.01 ppb. Barnes Engineering Co. **198**

**Posters.** Four display cartoons are available, serving to remind the individual of responsibilities in controlling pollution. Nalco Chemical Co. **199**

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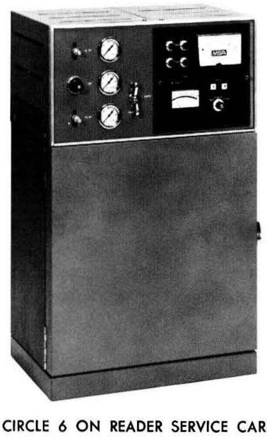

# BOOKS

**Mathematics for Water and Wastewater Treatment Plant Operators, Book 1: Fundamental; Book 2: Advanced.** Joanne Kirkpatrick. 490 and 435 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1973. $17.50 (each), paper.

The two books attempt to bridge the gap between the reasoning processes and the language of math, which exists for the student who has difficulty in mathematics. Book 1 is designed to give the student a fundamental understanding of the various calculations encountered in treatment processes. Book 2 includes concepts and problems of greater mathematical complexity.

**Third Annual Environmental Engineering and Science Conference Proceedings.** xv + 817 pages. Director of Professional Development, Speed Scientific School, University of Louisville, Louisville, Ky. 40208. 1973. $20, paper.

Reports to the environmental engineering community on the status of present environmental quality problems and the availability of pragmatic solutions to these problems. The 45 papers presented at the conference focused on: environmental legislation, environmental planning, water resources development, environmental impact analysis, air quality control, and other problem areas.

**Programming Environmental Improvements in Public Transportation.** Edmund J. Cantilli, xxix + 151 pages. Lexington Books, 125 Spring St., Lexington, Mass. 02173. 1974. $12.50, hard cover.

Seeks to change attitudes toward the value of the opinions, desires, and needs of the riding public. It discusses a method of distributing funds for the improvement of public transportation facilities in which public opinion plays an integral part in the development of an allocation index. The book is designed for the student of transportation as well as the policymaker.

**Aerosol Technology in Hazard Evaluation.** Thomas T. Mercer. xi + 394 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1973. $19.50, hard cover.

Prepared to provide information on the growing concern over inhalation of toxic particles. The book outlines techniques used to measure and produce toxic aerosols. It emphasizes the importance of measuring the distribution of toxic material as a function of the dynamic characteristics responsible for the deposition of particles in the respiratory tract.

**Models for Environmental Pollution Control.** Rolf A. Deininger, Ed. xi + 448 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. $24.50, hard cover.

Deals with the use of mathematical modeling and systems analysis techniques for the development of resources and the control of environmental pollution. An extensively researched survey, the book contains sections on water pollution control, air pollution control, solid waste disposal, noise control, and total environmental models.

**Ultimate Disposal of Wastewaters and their Residuals.** F. Eugene McJunkin, P. Aarne Vesilind, Eds. vi + 315 pages. Water Resources Research Institute, 124 Riddick Building, North Carolina State University, Raleigh, N.C. 27607. 1973. $8.00, prepaid; $10, if billed. Paper.

Record of proceedings of the National Symposium on Ultimate Disposal of Wastewaters and Their Residuals sponsored by the Research Triangle Universities in North Carolina and the U.S. Environmental Protection Agency's Region IV. The proceedings reflect interest in this important field. The papers examine treatment trends at present, and their alternatives.

**Proceedings of the International Symposium on Environmental Measurements.** Beckman Instruments. 150 pages. Beckman Instruments, 2500 Harbor Blvd., Fullerton, Calif. 92634. 1974. $15.

Proceedings of a 3-day symposium held in Geneva, Switzerland, October 1973, on the latest developments in the field of environmental measurement and related controls and regulations. Fifteen sessions included papers on environmental management, status of source measurement requirements and techniques in the U.S., chemical reactions in the atmosphere, and pollution abatement activities.

**Chemical Villains: A Biology of Pollution.** James W. Berry, David W. Osgood, Philip A. St. John. vii + 189 pages. C. V. Mosby Co., 3301 Washington Blvd., St. Louis, Mo. 63103. 1974. $5.75, paper.

First part of book discusses basic concepts involving ecosystems and biogeochemical cycles, aspects of cell physiology, and functions of tissues and organs of animals. Second part details many environmental contaminants and their actions on cells and tissues of organisms. Stresses that what contaminates our environment, eventually will contaminate humans.

**Coastal Ecosystems: Ecological Considerations for Management of the Coastal Zone.** John Clark, xiii + 178 pages. Publications Department, The Conservation Foundation, 1717 Massachusetts Ave., N.W., Washington, D.C. 20036. 1974. $4.00 paper; $7.95, hard cover.

First of a series of documents being prepared under contract from the National Oceanic and Atmospheric Administration's Office of Coastal Environment in an effort to provide technical assistance to decisionmakers involved with coastal zone management issues. Aims at a wide array of federal, state, and local officials, planners, and lay persons with interest in wise use of this resource.

**Applications of Commercial Oxygen to Water and Wastewater Systems.** Richard E. Speece, Joseph F. Malina, Jr., Eds. xiii + 368 pages. Center for Research in Water Resources, University of Texas, Austin, Tex. 78712. 1973. $12.50, hard cover.

Conference proceedings from the sixth Water Resources Symposium held by the University of Texas Center for Research in Water Resources. Seeks to provide a state-of-the-art review of the subject in order to provide engineers with the concepts and rational basis applicable for design and operation of commercial oxygen facilities.

**pH and p-Ion Control in Process and Waste Streams.** F. G. Shinskey. xvi + 259 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1973. $17.95, hard cover.

Offers complete guide to the design of a controllable effluent treatment plant. Book is intended for those engineers who must span several separate scientific disciplines to design and operate a waste treatment facility. Along with acids and bases, toxic pollutants such as cyanide, chromate, mercury, and phosphates also are considered.

**Remote Sensing: Techniques for Environmental Analysis.** John E. Estes, Leslie W. Senger, Eds. viii + 340 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1974. $11.50, hard cover.

Book is outgrowth and expansion of workshop readings offered at the 24th International Geographical Union meetings in Montreal, Canada, August 1972. It seeks to provide geographers and other scientists from developing nations with a basic introduction to the field of remote sensing. Could serve as a text for upper division undergraduates and to graduate students.

**Air Pollution Technology.** Dean E. Painter. xii + 283 pages. Reston Publishing Co., Inc., P.O. Box 547, Reston, Va. 22090. 1974. $13.95, hard cover.

Intended both as a college text for persons who plan to become involved in air pollution control technology and as an interdisciplinary program to inform all people of their responsibilities in conquering and controlling air pollution. Contains material condensed from numerous pamphlets, federal registers, and other documents of current origin. Each chapter lists references.

**Environmental Phosphorus Handbook.** Edward J. Griffith et al. xvi + 718 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1973. $34.95, hard cover.

A comprehensive study of phosphorus in the environment. Articles demonstrate that phosphorus in the environment occurs in many forms and performs an all but limitless number of complex functions. The element is viewed telescopically, beginning with studies of gigantic systems, followed by smaller and smaller subsystems until the smallest details are explored.

**Our Ecological Crisis: Its Biological, Economic, & Political Dimensions.** Grahame J. C. Smith, Henry J. Steck, Gerald Surette. ix + 198 pages. Macmillan Publishing Co., Inc., 866 Third Ave., New York, N.Y. 10022. 1974. $5.95, hard cover.

Seeks to be a "second generation" ecology book that draws on the disciplines of ecology, economics, and political science to produce a reflective, integrated test. Section I lays down a ecological framework. Section II explores the cultural and economic roots of the crisis and examines, in the light of modern economic theory, the structure and functioning of our economic system in relation to its ecological context.

**Introduction to Environmental Science.** Arthur N. Strahler, Alan H. Strahler, ix + 633 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1974. $15.95, hard cover.

Designed as an introductory text, book stresses the understanding of natural systems and processes of the earth and their implications for and impact on man. It focuses on this man—natural systems' interaction in both their geoscience and ecoscience aspects. Special attention is given to natural resources, their origin and occurrence, and the impact of their use.

**Taming the Last Frontier: A Prescription for the Urban Crises.** C. W. Griffin, Jr. xii + 260 pages. Pitman Publishing Corp., 6 East 43 St., New York, N.Y. 10017. 1974. $8.95, hard cover.

Contains suggestions for ameliorating the urban condition. The author believes we still have time to reverse present trends and resolve our urban crisis. He rejects the heavy stress on voluntary action, and points to the need for institutional, rather than personal, change. Seeks at least partial solutions to the problems of air pollution, water pollution, traffic congestion, population growth, slums, and suburban sprawl.

**Environmental Education at University Level: Trends and Data.** Centre for Educational Research and Innovation (CERI). 320 pages. OECD Publications Center, 1750 Pennsylvania Ave., N.W., Washington, D.C. 20006. 1973. $7.50, paper.

Partially based on the results of a Workshop on Environmental Education at University Level, organized in Tours, France, April 1971. It seeks answers to question: Will the universities be dynamic enough to create programs that effectively bridge theory and practice, and thereby involve the professions? And: Will the professions accept the challenge?

# MEETING GUIDE

**June 20–21** Washington, D.C.
**First Conference on Energy R&D.** Government Institutes, Inc.

Presentations will include Project Independence. *Contact:* GII, Suite 303, 4733 Bethesda Ave., N.W., Washington, D.C. 20014

**June 26–27** Washington, D.C.
**ASTM Symposium on Automatic Sampling and Measurement for Water Pollution Assessments.** American Society for Testing Materials

*Contact:* Jane B. Wheeler, ASTM, 1916 Race St., Philadelphia, Pa. 19103

**June 26–28** Ithaca, New York
**Water Quality Planning.** American Society of Civil Engineers

*Contact:* Herbert Hands, ASCE, 345 E. 47th St., New York, N.Y. 10017

**July 1–2** Golden, Colo.
**Water Resources Problems Related to Mining.** American Water Resources Association

*Write:* AWRA, 206 E. University Ave., Urbana, Ill. 61801

**July 1–5** Hampton, N.H.
**Environmental Sciences: Water.** Gordon Research Conferences

*Write:* Alexander Cruickshank, GRC, University of Rhode Island, Kingston, R.I. 02881

**July 7–12** Henniker, N.H.
**Methanol as an Alternate Fuel.** Engineering Foundation

*Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

**July 8–11** University Park, Pa.
**Environmental Engineering Specialty Conference.** American Society of Civil Engineers.

*Write:* ASCE, 345 E. 47th St., New York, N.Y. 10017

**July 8–12** Johnson, Vt.
**Fourth American Society for Testing and Materials Committee D-22 Meeting.** American Society for Testing and Materials

Theme is "The Concepts of Data Acquisition and Interpretation in Air Quality Monitoring." *Contact:* S. K. Kempner, Western Electric Co., 222 Broadway, New York, N.Y.

**July 9–11** Houston, Tex.
**1974 Summer Computer Simulation Conference.** American Institute of Chemical Engineers and others

*Write:* Carl Malstrom, Publicity Chairman, Rhodes Engineering Research Center, Clemson, S.C. 29361

**July 15–18** Newport Beach, Calif.
**Annual Meeting.** National Water Supply Improvement Association

*Write:* NWSIA, 10500 Ellis Ave., P.O. Box 8300, Fountain Valley, Calif. 92708

**July 15–19** Montreal, Canada
**Transportation Engineering Meeting.** American Society of Civil Engineers

*Write:* ASCE, 345 E. 47th St., New York, N.Y. 10017

**July 29–31** Columbia, Mo.
**Nuclear Methods in Environmental Research.** American Nuclear Society

*Write:* David Pettengill, 244 E. Ogden Ave., Hinsdale, Ill. 60521

**July 30–August 4** Seattle, Wash.
**Intersociety Conference on Environmental Systems.** American Society of Mechanical Engineers

*Write:* ASME, 345 E. 47th St., New York, N.Y. 10017

**August 4–9** Rindge, N.H.
**Engineering Coal Waste Disposal.** Engineering Foundation

Conference on "Urban Runoff-Quantity and Quality" will be held at same location August 11–16. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

**August 11–14** Syracuse, N.Y.
**Annual Meeting.** Soil Conservation Society of America

Theme is "Land Use-Persuasion or Regulation?" *Write:* SCSA, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

**August 18–21** Salt Lake City, Utah
**Seventy-eighth National AIChE Meeting.** American Institute of Chemical Engineers

*Contact:* Joel Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

## Courses

**June 17–18** Nashville, Tenn.
**Effluent Guidelines—Alternative Approaches.** Vanderbilt University

Fee: $150. *Contact:* J. A. Roth, Box 1574, Station B, Vanderbilt U., Nashville, Tenn. 37235

**June 24–26** Berkeley, Calif.
**Air Quality Impact Analysis for Application in Land-Use and Transportation Planning.** University of California

Fee: $90. *Write:* Dept. BD, U. of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

**June 24–28** Houghton, Mich.
**Thermal Pollution Control Workshop.** Michigan Technological University

Fee: $250. *Write:* T. G. Ellis. Continuing Education, MTU, Houghton, Mich. 49931

**June 24–28** Ithaca, N.Y.
**Industrial Wastewater Control.** Cornell University

*Contact:* College of Engineering, Cornell U., Ithaca, N.Y. 14850

**June 26–28** Macon, Ga.
**Environmental Health Management: Measurement and Sampling Techniques.** International Safety Academy

Offered at different times. *Write:* K. E. Barenklau, International Safety Academy, 1021 Georgia Ave., Macon, Ga. 31201

**July 1–26** Boston, Mass.
**Summer Institute on Air Pollution Management.** Harvard School of Public Health

Aimed at increasing the understanding and teaching skills of faculty members in environmental science fields. Enrollment limited to thirty. *Write:* Dade Moeller, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115

**July 8–26** Cambridge, Mass.
**Nuclear Power Reactor Safety.** Massachusetts Institute of Technology

*Contact:* Director, Summer Session Office, Rm E19-356, MIT, Cambridge, Mass. 02139

**July 14–27** Fort Collins, Colo.
**International School for Environmental Management.** Westinghouse Electric Corp.

*Write:* J. H. Wright, Westinghouse Electric Corp., Westinghouse Bldg., Pittsburgh, Pa. 15222

**July 15–19** Boston, Mass.
**Evaluation and Control of Occupational Hazards.** Harvard School of Public Health

*Write:* M. W. First, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass 02115

**July 15–19** Detroit, Mich.
**Water Supply and Treatment.** Wayne State University

Fee: $275. Course on water pollution control will run the week following, and course on industrial waste treatment will run the third week. *Contact:* College of Lifelong Learning, Wayne State U., Detroit, Mich. 48202

**July 15–19** Cleveland, Ohio
**Industrial Noise Control Seminars.** B&K Instruments, Inc.

Fee: $200. *Write:* Bill Rhodes, Director of Communications, B&K Instruments, 5111 W. 164th St., Cleveland, Ohio 44142

**July 17–19** Washington, D.C.
**Environmental Impact Statements.** George Washington University

Fee: $250. *Contact:* Continuing Engineering Education Program, GWU, Washington, D.C. 20006

## International

**June 17–19** Basle, Switzerland
**Annual Symposium on Recent Advances in Analytical Chemistry of Pollutants.** EPA and others

*Contact:* D. M. Hercules, Dept. of Chemistry, U. of Georgia, Athens, Ga. 30602

**June 23–26** Houston, Tex.
**International Waste Equipment and Technology Exposition.** National Solid Wastes Management Association

*Write:* NSWMA, 1730 Rhode Island Ave., N.W., Washington, D.C. 20036

**June 23–28** Washington, D.C.
**International Symposium on Metrication.** American Society for Testing Materials and others

*Write:* ASTM, 1916 Race St., Philadelphia, Pa. 19103

**June 24–27** Algiers, Algeria
**LNG-4: Fourth International Conference on Liquefied Natural Gas.** International Gas Union and others

*Contact:* A. F. Rinella, Industry & Public Information, Institute of Gas Technology, 3424 S. State St., Chicago, Ill. 60616

**June 24–28** Paris, France
**Symposium on Recent Advances in the Assessment of the Health Effects of Environmental Pollution.** Commission of the European Communities, EPA, and WHO

*Contact:* J. Smeets, Secretary General for the Symposium, 29 Rue Aldringen, Luxembourg

**July 1–5** Paris, France
**First World Congress of Environmental Medicine and Biology.** International Association of Medicine and Biology of Environment and others

*Write:* Richard Abbou, 115 rue de la Pompe, 75116, Paris, France

**July 14–20** Seattle, Wash.
**Fifth International Congress of Radiation Research.** International Association for Radiation Research

*Write:* W. K. Sinclair, Secretary-General, 5th I.C.R.R., Argonne National Lab., Argonne, Ill. 60439

**July 29–31** Columbia, Mo.
**Second International Conference on Nuclear Methods in Environmental Research.** University of Missouri

*Write:* Dr. James R. Vogt, Environmental Trace Substances Research Center, U. of Missouri, 1020D-Engineering Ext., Columbia, Mo. 65201

**August 8–20** Moscow, U.S.S.R.
**Soil Science 1974.** International Congress of Soil Scientists

*Write:* Welt East European Exhibit Management, Div. of Welt International Corp., 180 N. Michigan Ave., Chicago, Ill. 60601

**August 12–14** Ontario, Canada
**Seventeenth Conference on Great Lakes Research.** International Association for Great Lakes Research

*Contact:* Dr. Rodgers, Canada Centre for Inland Waters, Box 5050, Burlington, Ont., Canada

**August 17–22, 1975** Kingston, R.I.
**Third International Biodegradation Symposium.** Office of Naval Research and others

Theme is "Man, Biology, Materials." *Contact:* R. W. Traxler, 231 Woodward Hall, U. of Rhode Island, Kingston, R. I. 02881

*(continued on page 542)*

**August 19–30** Bucharest, Rumania
**World Population Conference.** United Nations

Topics will include relations between population, resources and environment. *Contact:* Office of the Secretary General, World Population Conference, United Nations, New York, N.Y. 10017

**September 8–14** The Hague, The Netherlands
**First International Congress of Ecology.** International Union of Biological Sciences and others

*Contact:* Human Adaptability Coordinating Office, 513 Social Science Bldg., University Park, Pa. 16802

**September 9–12** Chicago, Ill.
**International Pollution Engineering Exposition and Concurrent Congress.** Clapp and Poliak Inc.

*Contact:* Clapp & Poliak Inc., 245 Park Ave., New York, N.Y. 10017

**September 9–12** Paris, France
**Symposia on Effects of Man on the Hydrological Cycle and on Flash Floods.** UNESCO and others

*Write:* U.S. National Committee, International Hydrological Decade, National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418

**September 9–13** Paris, France
**1974 Conference.** International Association on Water Pollution Research

*Contact:* S. H. Jenkins, 156/170 Newhall St., Birmingham, B31SE, England

**September 11–14** Geneva, Switzerland
**Eurosaf 74.** Exhibition Managements Ltd. and others

Focuses on significant developments in the fields of industrial safety and health. *Write:* Exhibition Managements Ltd., 159 Mortlake Rd., Kew, Surrey, England

**September 15–21** Munich, West Germany
**Joint AIChE–Technical Management Society Meeting.** American Institute of Chemical Engineers

*Contact:* Joel Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

**September 22–27** Detroit, Mich.
**World Energy Conference.** World Energy Conference

*Write:* A. G. DeLorenzo, WEC, 234 State St., Rm. 1000, Detroit, Mich. 48226

**September 30–October 2** Washington, D.C.
**Inter-Noise 74.** Institute of Noise Control Engineering

*Contact:* J. C. Johnson, Applied Research Lab., Penn State University, P.O. Box 30, State College, Pa. 16801

## Call for Papers

**June 30 deadline**
**Seventh Mid-Atlantic Industrial Waste Conference.** Drexel University

Conference will be held in Philadelphia on November 12–14. Emphasis on topics re air/water pollution control and solid waste disposal. *Write:* Dr. La Grega, Institute of Environmental Studies, Drexel U., Philadelphia, Pa. 19104

**September 1 deadline**
**IFAC/75.** International Federation of Automatic Control

Conference will be held August 24–30, 1975. *Write:* IFAC/75 Secretariat, 400 Stanwix St., Pittsburgh, Pa. 15222

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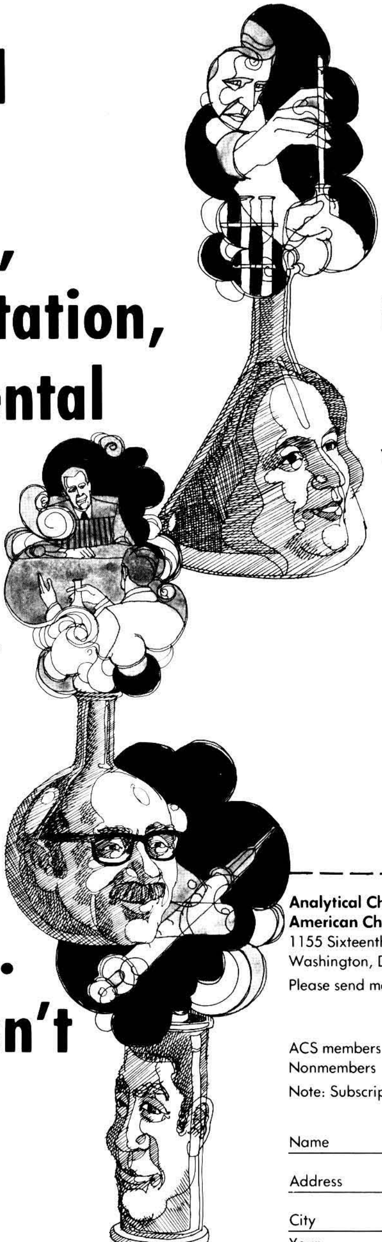

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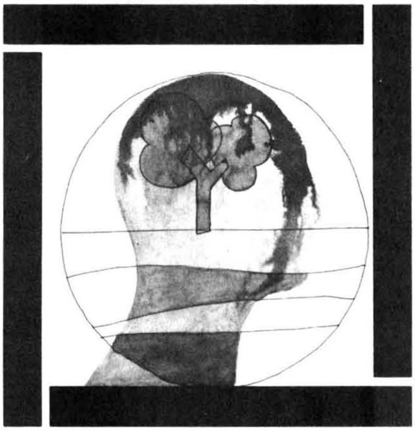

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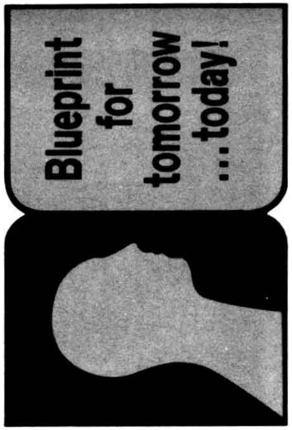

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(1) Rodes, C. E., Div. of Environ. Chem., 167th Meeting, ACS, Los Angeles, Calif., March 1974.

(2) Environmental Protection Agency, Water Quality Office, Cincinnati, Ohio, "Methods for Chemical Analysis of Water and Wastes," pp 246–57, 1971.

(3) Cottrell, F. G., U.S. Patent 895,729 (1908).

(4) Sparks, L. E., "The effect of Scrubber Operating and Design Parameters on Collection of Particulate Air Pollutants," PhD Thesis, Univ. of Washington, Seattle, Wash., 1971.

(5) Heicklen, J., Westberg, K., Cohen, N., in "Chemical Reactions in Urban Atmospheres," C. S. Tuesday, Ed., p 35, American Elsevier, New York, N.Y., 1969.

(6) Hecht, T. A., Seinfeld, J. H., *Environ. Sci. Technol.*, **6**, 47 (1972).

(7) Gay, B. W., Jr., Bufalini, J. J., *ibid.*, **5**, 422 (1971).

(8) U.S. Dept. of Health, Education and Welfare, Public Health Service, Cincinnati, Ohio, "Selected Methods for Measurement of Air Pollutants," 1965.

# CURRENT RESEARCH

## Composition and Size Distributions of Atmospheric Particulate Matter in Boston Area

**Ernest S. Gladney, William H. Zoller, Alun G. Jones,[1] and Glen E. Gordon[2]**
Department of Chemistry, University of Maryland, College Park, Md. 20742

■ Samples of atmospheric particulate matter were collected with a cascade impactor at three sites in the Boston area and analyzed for 18 elements by instrumental neutron activation analysis. As expected, Na and Cl have typical marine aerosol size distributions, and Br and V have small-particle distributions resulting from leaded gasoline combustion and residual oil combustion, respectively. Distributions of remaining elements can be classed as large-particle (Al, Sc, Th, and Fe), small-particle (Se, Sb, and Zn), and mixed component (Co, Mn, and Ce). The size distributions, even within these classes, are so distinctive that cascade impactors can be used to identify sources of the elements in urban areas when emissions from various types of sources have been characterized by these same methods.

Over the past several years there has been increasing concern about the health effects, damage to vegetation and materials, and reduced visibility caused by atmospheric particles generated by man's activities. To help identify the sources and behaviors of particles and to determine the respirable size fractions for particles bearing toxic elements, it is important to measure both the size distributions and compositions of particles in urban air.

The only available instrument for simultaneous determination of size distributions and chemical composition of particles is the cascade impactor. Cascade impactors and the parameters involved in their separation efficiencies for particles have been described elsewhere (Brink, 1958; Mitchell and Pilcher, 1959; Andersen, 1966; Lundgren, 1967; Pilat et al., 1970; Lee and Goranson, 1971; Soole, 1971; Gordon et al., 1973a; Gladney et al., 1973b). Size distributions of particles to which various elements are attached are determined by analysis of the separate size portions collected.

The major problem of chemical analyses of the size fractions is that cascade impactors collect very small amounts of material. Many impactors now in use sample air at the rate of about 1–2 $m^3/hr$, so that in a 24-hr sampling period only about 10–50 $\mu g$ of any one element will be present, distributed over the several collection surfaces. Often one wishes to study elements that are present in very low atmospheric concentrations, say 10 $ng/m^3$, in which case, only 0.25–0.5 $\mu g$ of the element is present.

There have been enormous improvements in the analytical techniques that can be used; particularly, the development of instrumental neutron activation analysis (INAA). Zoller and Gordon (1970), for example, used INAA to determine concentrations of up to 24 elements in individual air samples in 1- to 2-mg filter samples of particulate material. With the collection of samples with cascade impactors and analysis by INAA one should be able to characterize particulates from major types of sources and observe their interactions after release.

Several investigators have previously used cascade impactors to measure size distributions of particles bearing various elements in urban and rural areas (Corn and DeMaio, 1964; Lee and Patterson, 1969; Nifong and Winchester, 1970; Lee, 1972; Lee and Goranson, 1972; Lee et al., 1972). In this study of Boston area aerosols, we have shown that, for elements whose sources are well-known, the observed size distributions are in good agreement with known size distributions, or projected size distributions based on known atmospheric injection mechanisms. For other elements whose sources are not clearly established, we observe several types of size distributions that are sufficiently distinctive that they could be used as a means of source identification if more data on size distributions of particles from specific types of sources were available.

### *Experimental Methods*

**Cascade Impactor.** Samples were collected using a six-stage Scientific Advances Co. cascade impactor (Mod. CI-S-6) connected to a Gelman Air-Sampling Kit. The impactor stood vertically, with a polyethylene shield above it to prevent collection of very large debris or precipitation. The collectors were high-purity polyethylene films of about 5 $cm^2$ in area mounted on circular glass slides.

Collection efficiencies of the Scientific Advances (SA) impactor for particles of various size have been measured by Mitchell and Pilcher (1959). Their values of the 50% effective cutoff diameter (ECD) for each stage are listed in Table I. These calibrations apply to spherical particles of unit density. Since most ambient aerosols probably do not have these characteristics, there is some uncertainty about the size fractions actually collected. Also, the sizes and densities of hygroscopic particles depend on relative humidity (Duce et al., 1967).

Two other effects can distort the observed particle size distributions: wall losses and re-entrainment of particles. Studies of impactor characteristics indicate that these effects are often quite serious (Mitchell and Pilcher, 1959; O'Donnell et al., 1970; Lundgren, 1967, 1972; Gordon et al., 1973a). Although the SA impactor has a lower flow rate (0.75 $m^3/hr$) than most other impactors, we chose it because our studies showed that it produces less distortion

**Table I. Effective Cutoff Diameters for Scientific Advances Impactor**

| Stage | ECD, $\mu$[a] | Stage | ECD, $\mu$[a] |
|---|---|---|---|
| A | 16 | D | 2 |
| B | 8 | E | 1.0 |
| C | 4 | F | 0.5 |

[a] Mitchell and Pilcher (1959).

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[2] To whom correspondence should be addressed.

**Table II. Conditions During Collections of Samples**

| Site | Sample | Date | Wind<br>Velocity, knots | <br>Direction | Temp, °C | Rel. humidity, % | Remarks |
|---|---|---|---|---|---|---|---|
| MIT-1 | #1 | Feb. 6–7 | 2–7 | Strongly variable | −2 to 0 | 69–80 | Trace precipitation |
| | #2 | Feb. 7–8 | 3–6 | Strongly variable | −3 to +3 variable | 65–81 | |
| | #3 | Feb. 8–9 | 3–6 | SE-SW | −1 to +6 | 53–74 | |
| MIT-2 | #1 | Feb. 15–16 | 3–16 | N-WSW | −3 to +1 | 47–87 | Trace precipitation |
| | #2 | Feb. 17–18 | 2–10 | N-E | −3 to +2 | 70–81 | |
| | #3 | Feb. 21–22 | 9–15 | W | −5 to +1 | 41–54 | |
| RT-128 | #1 | Mar. 2–3 | 6–10 | NW-SW | −4 to +2 | 55–81 | 0.03″ ppt |
| | #2 | Mar. 3–4 | 2–12 | N-E | −3 to +2 | 44–80 | |
| | #3 | Mar. 6–7 | 10–14 | N | −1 to +3 | 65–87 | |

**Table III. Averages of Summations of Elemental Mass Concentrations per Stage Compared with Other Whole-Filter Measurements**

| Element | Concentration, ng/m³<br>Av of 6 runs at MIT sites | <br>Av of 3 runs at RT-128 | <br>Filter data[a], MIT-1 site | <br>NASN[b] 1968 |
|---|---|---|---|---|
| Na | 2340 | 1560 | 1480 | |
| Al | 1320 | 870 | 1630 | |
| Cl | 2300 | 1570 | 590 | |
| Sc | 0.25 | 0.26 | 0.36 | |
| V | 860 | 86 | 980 | 620 |
| Mn | 30 | 20 | 30 | 10 |
| Fe | 1370 | 820 | 1480 | 1900 |
| Co | 2.3 | 0.62 | 1.3 | |
| Zn | 340 | 100 | 260 | 300 |
| Se | 4.4 | 4.9 | 1.4 | |
| Sb | 7.4 | 1.3 | 12 | |
| Ce | 4.1 | 2.3 | 3.0 | |
| Yb | 0.03 | 0.04 | 0.02[c] | |
| Lu | 0.003 | 0.002 | 0.01[c] | |
| Hf | 0.05 | 0.03 | 0.03[c] | |
| Ta | 0.06 | 0.05 | . . . | |
| Th | 0.11 | 0.13 | 0.03 | |

[a] Gladney et al. (1973a) unless otherwise noted. [b] Data from the National Air Surveillance Network (Akland, 1973). [c] Zoller and Gordon (1970).

of the particle-size distribution than other types of impactors (Gladney et al., 1973b). Other studies (e.g., Wesolowski, 1973) have shown that nonhygroscopic particles (e.g., rock dust) tend to have severe bounce-off problems when collected with Lundgren impactors, especially during periods of low humidity, that can be prevented by application of a sticky substance to the collection surfaces. Our studies show that bounce-off is much less severe with use of the SA impactor.

**Sample Collection.** Samples were collected at the three sites in the Boston area indicated on the map of Figure 1. The first, MIT-1, was on the roof of the two-story MIT Nuclear Chemistry Building located about three blocks from the Charles River in an area of mixed activities (education, commercial, and light industry), with high traffic density. The second site, MIT-2, was on the roof of the 19-story MIT Green (Earth Sciences) Building about 100 m above ground level in the middle of the campus. The third site, RT-128, was in the lawn of a private home in Wellesley, a suburb about 12 miles to the west of Boston and about 1 mile west of the heavily traveled circumferential highway, Route 128. Wellesley is largely a residential city, with few major pollution sources other than automobiles and home-heating units.

Three sets of samples were taken at each site during February and March 1970. As only one impactor was available, samples at the various sites were taken at different times under somewhat different conditions. A summary of the weather conditions during the 24-hr sample-collection periods is given in Table II.

**Analyses.** The INAA method used was almost the same as that reported previously for filter samples of particulate material (Zoller and Gordon, 1970). Each of the six polyethylene films from a collection experiment was sealed in a precleaned polyethylene bag and irradiated in a reactor simultaneously with a monitor solution, containing known amounts of the elements of interest. Irradiations were done in the MIT reactor ($\phi = 2 \cdot 10^{13}$ n/cm²-sec) and the National Bureau of Standards reactor ($\phi = 6 \cdot 10^{13}$ n/cm²-sec). Aliquots of the irradiated monitor solution were pipeted onto Millipore filter material that approximated the size and shape of the polyethylene-film samples in order to give the same geometrical configuration during counting.

Spectra of the $\gamma$-rays emitted by the samples were observed several times after irradiation with large (26–65 cm³) high-resolution Ge(Li) detectors (FWHM for $^{60}$Co routinely 2.2 keV) coupled to 4096-channel pulse-height analyzers.

## *Results*

The observed particle-size distributions for the various elements are shown below in Figures 3 to 9. The mass of the given element per stage per m³ of air sampled is plotted vs. the stage designation with Stage A (the largest particles) at the right and Stage F (smallest particles) at the left.

Before considering the detailed interpretation of the results, we would emphasize the excellent ability of the impactor to separate particles of various sizes. In the particle size distributions of Figures 5, 6, and 9, we see that in the most extreme case, Al is differentiated by a factor of about $10^3$ between intermediate stages and Stage F, whereas elements such as Zn, Sb, and Se are often differentiated by a factor of $10^2$ between Stage F and Stage A, giving a relative differentiation of up to a factor of $10^5$ between various elements.

Absolute weights are not given for Br in Figure 4 because of difficulties with the Br monitor. During several-hour irradiations, the monitor becomes warm enough to lose volatile Br. Thus, the absolute magnitudes of each set of points have no significance, but the points from a particular run are good relative to one another.

To give an estimate of the composition of aerosols in the Boston in-town and suburban areas, we have listed average values of the summations of elemental concentrations on the six impactor stages in Table III. Separate averages for the three RT-128 experiments and the six MIT experi-

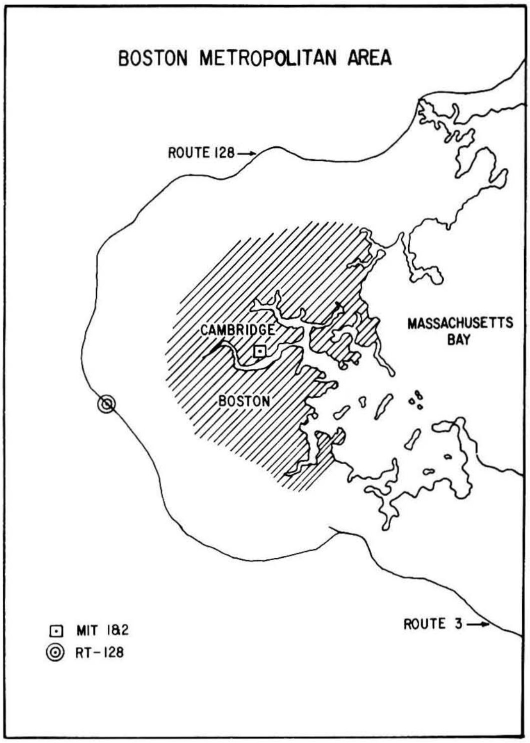

**Figure 1.** Map of the Boston area showing sampling sites
In general, the high population density is located in the shaded region. Downtown Boston is just across the Charles River Basin to the ESE of MIT

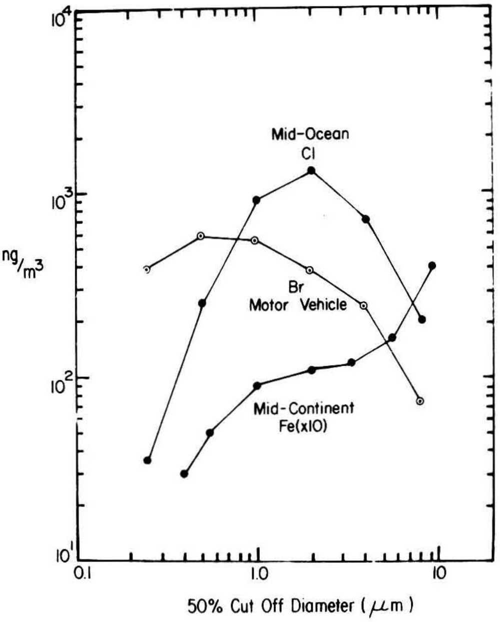

**Figure 2.** Typical size distributions for continental dust in remote areas observed by Rahn (1971) with an Andersen sampler, for marine aerosols observed in Hawaii by Duce et al. (1967) with a Scientific Advances cascade impactor, and auto exhaust particles by Ondov (1973) with a Scientific Advances impactor

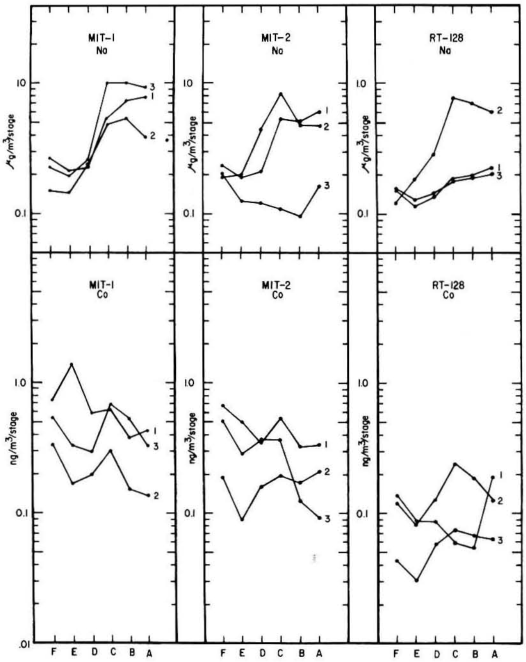

**Figure 3.** Size distributions obtained for Na and Co in the Boston area

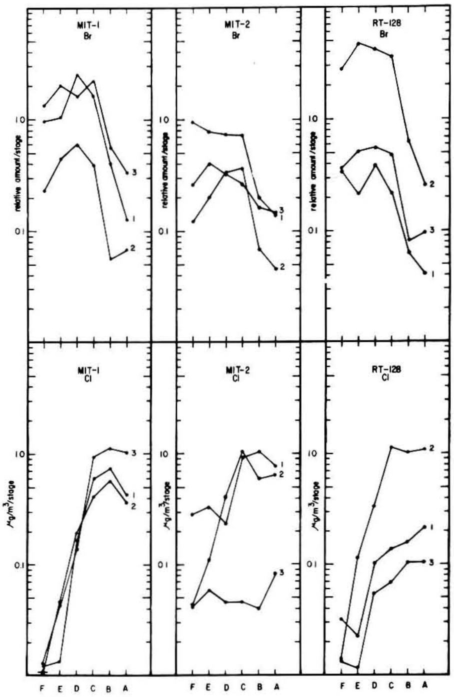

**Figure 4.** Size distributions obtained for Br and Cl in the Boston area

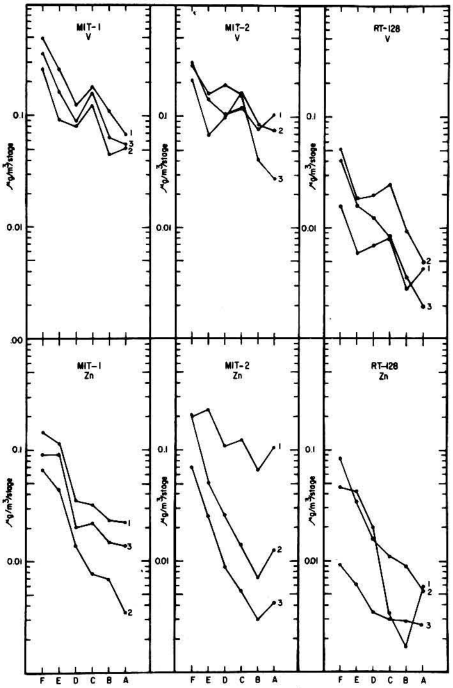

**Figure 5.** Size distributions obtained for V and Zn in the Boston area

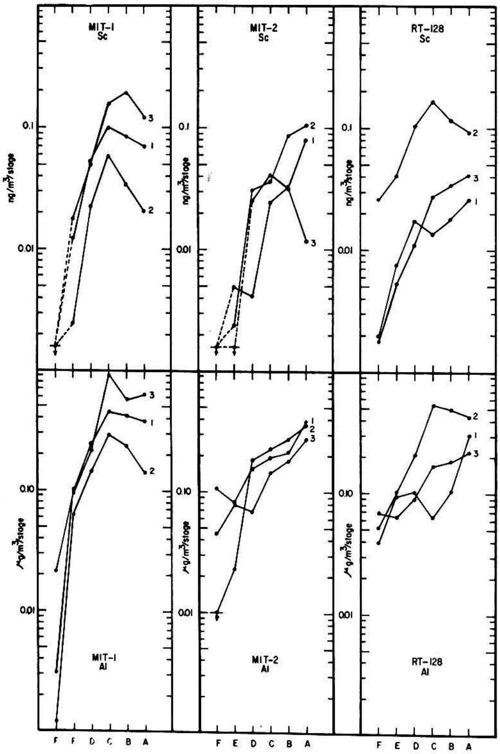

**Figure 6.** Size distributions observed for Sc and Al in the Boston area

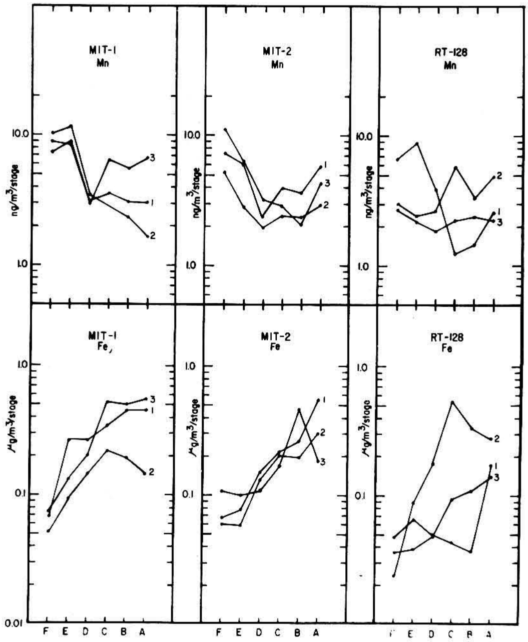

**Figure 7.** Size distributions observed for Mn and Fe in the Boston area

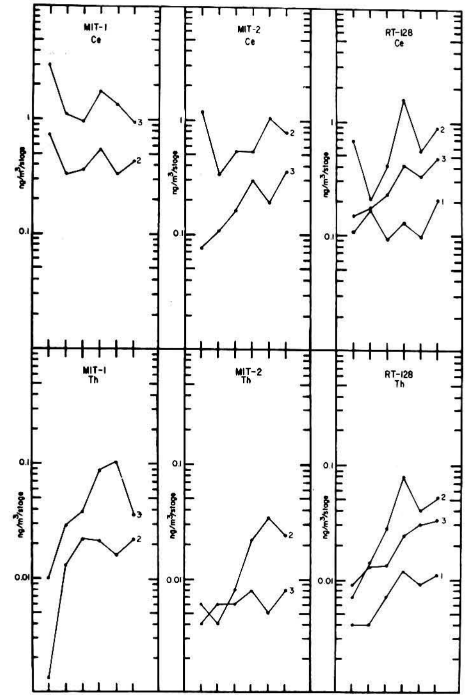

**Figure 8.** Size distributions observed for Ce and Th in the Boston area

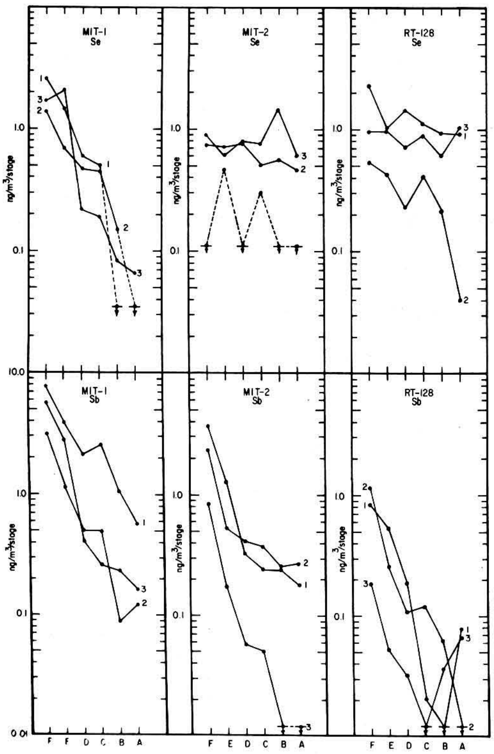

**Figure 9.** Size distributions observed for Se and Sb in the Boston area

ments are given. It should be noted that we did not use back-up filters on the impactors; thus, the summations include only particles large enough to be collected on the impactor—i.e., $d > 0.4$ μm. The error introduced for large-particle elements such as Fe and Al is quite small, but for predominantly small-particle elements such as Se and Br, a substantial fraction (perhaps 20–30%) may pass beyond the last impactor stage. For comparison with the summations, we also list concentrations previously determined from whole filter analyses. The generally good agreement between filter and impactor data, especially for small-particle elements such as V, suggest that the fraction of material passing through the entire impactor is small.

*Interpretation of Results*

To make a detailed interpretation of data of the sort obtained, one would wish to have available knowledge of: (a) size distributions of particles originating from various important types of sources and (b) the relative magnitudes of sources of each element. At present, information on both points is far from complete. Regarding point (a), it is known that mechanical processes such as abrasion and wind erosion release particles of predominantly large size and that vaporization followed by cooling and condensation yields particles of very small size. However, the only sources whose particles are well characterized according to size are marine aerosols (Duce et al., 1967), continental background particles (Rahn, 1971), and lead- and halogen-bearing particles from gasoline combustion in automobiles (Ondov, 1973) (see Figure 2). Beyond that, it is known that aluminosilicate fly ash particles from coal combustion are of large size as frequently observed by microscopy but volatile elements in coal are probably deposited on small particles (Natusch, 1974). Little is known about particles produced by other important sources such as oil combustion, incineration of trash, and most types of industries. The Boston area has sizable particulate contributions from the first two of those sources, but very little from industry (U.S. Dept. of HEW, 1968; Massachusetts, 1968; Morgenstern et al., 1970).

Regarding point (b) above, we (Gordon et al., 1972) and others (Miller et al., 1972; Friedlander, 1973) have attempted to resolve patterns of elemental concentrations on urban particulates into components originating from different types of sources such as coal and oil combustion, automobiles, marine aerosols, and wind erosion of soil. Elemental patterns of the components are usually assumed to be the same as the source materials—i.e., seawater, oil, local or worldwide average soil, the ethyl fluid added to gasoline, and whole coal or fly ash collected in precipitators of coal-fired plants.

Although resolutions of this type often achieve a semiquantitative self-consistency for many elements, they often fail by orders of magnitude to account for observed concentrations of several elements, especially Zn, Cd, Se, and Sb. The major reasons for these failures are fairly obvious: (1) the lack of information about certain types of sources such as incinerators and industries that make important particulate contributions in many areas and (2) the almost total absence of knowledge about the modification of the elemental concentration pattern when a fuel undergoes combustion. Regarding point (2), studies of the Allen steam plant by Bolton et al. (1973) have shown that there are marked differences of concentration patterns between coal entering the plant and suspended particles collected beyond the electrostatic precipitator. A number of chalcophile elements are enriched by factors of three to ten in the emitted particles relative to lithopile elements such as aluminum (Gordon and Zoller, 1973; Gordon et al. 1973b). One element, selenium, was enriched by a factor of 10,000. Even compositions of particulates collected in the stacks of major pollution sources may not be sufficient for resolutions of urban particulates, as the particles may be further modified by fallout and condensation of volatile species as emissions move up the stack and into the nearby ambient air. Thus, complete and accurate resolutions will become possible only after much more detailed analyses are made of particles released by the several types of important sources.

Although it is not possible to establish the relative magnitudes of the various sources for all the elements observed, those of several elements are known well enough to serve as a test of the applicability of size measurements. For several of the elements whose sources are not known, the observed size distributions place definite limits on the natures of their sources. In the following paragraphs we discuss the observed size distributions of particles bearing various elements in relation to the sources predicted for the elements.

*Elements from Known Sources*

**Sodium and Chlorine.** The cascade-impactor data for sodium and chlorine are shown in the upper half of Figure 3 and the lower half of Figure 4, respectively. The major portions of these elements undoubtedly originate from marine aerosols as in most coastal areas. The shapes of the size distribution curves for Cl for all runs except MIT-2-#3 and RT-128-#1 and #3 are in general agreement with the marine aerosol data of Duce et al. (1967) shown in Figure 2. Also, there is a strong correlation between Na and Cl. When winds were from inland directions between

N and SW (Runs MIT-2-#3 and RT-128-#1 and #3) the concentrations of Na and Cl were abnormally low and their size distributions flatter than for the other runs. It should be noted that the Na/Cl ratio, especially for the smallest particles, is noticeably greater than the seawater ratio of 0.55. Measurements of Na/Cl over land areas invariably show a deficiency of Cl relative to seawater, even in an area such as Los Angeles which is on a coast and has prevailing sea breezes (Miller et al., 1972). Apparently reactions of acids or oxidizing agents with Cl on particles in polluted air masses releases Cl to the gaseous state (see, for example, Cadle, 1972).

**Bromine.** Although Br is chemically similar to Cl, we see in Figure 4 that the size distributions for the two elements are quite different, Br being more predominantly associated with small particles. This is in agreement with the general finding that most Br in urban areas originates from automobile exhaust (see, for example, Duce et al., 1965; Moyers et al., 1972).

**Vanadium.** It has previously been shown that the unusually large atmospheric concentrations of vanadium in Boston and other northeastern U.S. cities result from combustion of residual oil (Zoller et al., 1973). As one would expect for such a high-temperature combustion source, the vanadium-bearing particles are preferentially of small size (Figure 5). The only uncertainty about the V distributions is the origin of the secondary peak observed on Stage C in most of the distributions. It is observed with such consistency that it cannot be dismissed as an experimental artifact; however, we have no obvious explanation for its presence. It's most unlikely that there is any additional source of V of magnitude comparable with that of residual oil (Zoller et al., 1973).

### *Other Elements*

Sources of the remaining elements are not as well-known as those of the four elements discussed above. We have grouped these other elements according to the general shapes of their size distributions—i.e., those that favor large particles, those attached to small particles, and those having both large- and small-particle components.

**Large-Particle Elements.** Particles bearing the elements Al, Sc, Fe, and Th are predominantly of large size (Figures 6 to 8). The most likely sources of large particles in Boston are fly ash particles from coal combustion and windblown soil and rock dust. Furthermore, these would be probable sources for the lithophile elements Al, Sc, and Th. The distributions of Al and Sc are so similar to each other that they surely originate from the same sources in about the same relative proportions.

Although the Fe distributions also favor large particles, most of them are distinctly different from those of Al and Sc. The curves for Al and Sc drop off very sharply at the small-particle end of the size spectrum, whereas the slopes are much shallower for the Fe curves. The Al and Sc distributions, especially at the MIT-1 site, appear to be quite different from those of continental weathering particles as shown in Figure 2. This probably means that much of the in-town Al and Sc are produced by local sources, possibly coal combustion as modified by electrostatic precipitators (which could account for the downturn at the large-particle end). The Al and Sc distributions obtained at Sites MIT-2 and RT-128 are more similar to continental weathering patterns.

Although the Fe patterns, in general, have an appearance similar to those of continental weathering, this may be fortuitous for the in-town sites. Much of the Fe undoubtedly originates from the same sources as Al—e.g., coal combustion. However, the size distribution of Fe-bearing particles from coal combustion may not be the same as for Al-bearing particles from the same source. Aluminum in coal is mainly present in aluminosilicate particles, whereas much of the Fe is in the form of sulfides. Iron in the latter form may be vaporized, followed by condensation on small particles, which would account for the observed greater number of small particles bearing Fe, as well as the enrichment of Fe relative to Al brought about by coal combustion (Gordon and Zoller, 1973). Admittedly, these suggestions are highly speculative and can be tested only by studies of particles from specific major sources. The main point that has been shown is that particles bearing two major elements, Al and Fe, which occur with comparable concentrations in many materials, display quite recognizably different size distributions.

The size distributions for Th-bearing particles are intermediate between those of Al and Fe, perhaps being somewhat more similar to the curves for Al.

**Small-Particle Elements.** In addition to vanadium discussed above, the size distributions for particles containing Zn, Se, and Sb strongly favor small diameters (Figures 5 and 9). The size distributions suggest that all are released primarily by vaporization followed by condensation. Selenium and Sb are so volatile that they could be vaporized by combustion of many materials such as coal, oil, or refuse. Although Zn is much less volatile than those elements, it is apparently also injected into the atmosphere after being vaporized. Friedlander (1973) has suggested tire dust as a major source of Zn in the Los Angeles atmosphere. However, since tire dust is surely created by abrasion, this suggestion is not consistent with the small-particle distribution that we observe for Zn in Boston. Apparently Zn originates from a combustion process. If major amounts of Se, Sb, or Zn originate from residual oil combustion, it is interesting to note that none of their size distributions shows much indication of a secondary peak as is observed for V.

**Mixed Size Distributions.** As shown in Figures 3, 7, 8, the size distributions for Co, Mn, and Ce show both small- and large-particle components, indicating that each of those elements originates from two or more processes of comparable magnitude. For Co, the drop-off in magnitude of the entire curve between Site MIT-1 and RT-128 is similar to that of V, so the small-particle component of the latter is probably due to oil combustion. Little can be said about the large-particle component, except that it is more similar in shape to the Al curves than those of Fe. On the other hand, the large-particle component for Mn appears to be more similar to that of Fe. The most interesting feature of the Ce curves is the fact that many show definite evidence of a small-particle component, despite the fact that Th, which is chemically rather similar, does not.

The samples were also analyzed for Yb, Lu, Ta, and Hf, whose summations are listed in Table III. However, analytical uncertainties for these elements are so large that we have not shown the size distribution curves for them. For the most part, the curves are either almost flat or they show a predominance of large particles.

### *Summary and Conclusions*

The Scientific Advances cascade impactor used in this work provided excellent separations of particles of different size as shown by the sharp contrast in size-distribution curves obtained for different elements.

For elements from known sources, we find the expected size distributions: marine aerosol distributions for Na and Cl, and predominantly small-particle distributions for Br from auto exhaust and V from residual oil combustion.

However, the V distributions exhibit a secondary peak, as yet unexplained, at intermediate sizes.

Size distribution curves for elements whose sources are not well-established can be divided into the following broad classes: predominantly large-particle (Al, Sc, Th, and Fe); preferentially small-particle (Se, Sb, and Zn); and mixed small- and large-particle distributions (Co, Mn, and Ce).

These results demonstrate that cascade impactor measurements with the use of a sensitive analytical technique such as INAA are a powerful tool for the determination of origins and behavior of elements attached to particulates in urban areas. Not only can the classifications of size spectra noted above be made, but one can also observe differences between elements within those classes—e.g., the Fe curves are distinctly different from those of Al and Sc.

To exploit these techniques in the study of particles in urban areas, one should now study particulates from known sources with use of the same methods.

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# Determination of Particle Size Distribution of Oil-in-Water Emulsions by Electronic Counting

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■ The particle size distribution of a hydrocarbon-in-water emulsion was determined by a Coulter counter model T. Dilution of the emulsion prior to the measurement resulted in a large decrease in particle numbers for the size range studied—i.e., 0.75–12.5 μ. This decrease in numbers after dilution was time-dependent and was attributed to the dissolution of the oil particles into the diluting electrolyte solution. Prior saturation of the electrolyte solution with hydrocarbon and a method of zero-time extrapolation are suggested to obtain a correct particle size distribution.

Particle size distributions of oil-in-water (O/W) emulsions are useful in studies of general and rheological properties of oil emulsions (Sherman, 1968) in the laboratory and in the environment. Coulter counting (Coulter Electronics, Hialeah, Fla.), by which large numbers of particles can be sized automatically and very rapidly, has usually been preferred over optical methods. The purpose of this paper is to illustrate various problems in using the Coulter counter, in particular the time dependency of the particle count after diluting the O/W emulsion with electrolyte solution. To determine the correct size distribution, prior saturation of the electrolyte solution with oil and zero-time extrapolation are proposed.

Problems in the application of the Coulter counter are three.

**Background Noise.** It was found that random background noise in the submicron range occurred, apparently because of electrical and mechanical interferences. Ultimately, low and reproducible background count could be attained by placing the counter in an isolated room and by shielding the sample stand (manometer) of the counter with copper screen.

**Limited Size Range of Aperture Tube.** The problem arose mainly from the emulsion system used in this study. The size of the oil particles ranged from submicron to about 15 μ and, depending on the O/W ratio, concentration of surfactant, and the treatment of emulsions, some oil particles larger than 15 μ were also observed. With such a broadly dispersed system, a two-tube technique should be employed. However, methods of separating oil particles dispersed in water can hardly give a satisfactory quantitative analysis with such a two-tube technique. Up until now, only one 30-μ aperture tube has been used in this study. This tube is recommended for the range 0.5–12.5 μ (manual of Coulter counter model T). However, it was found that electronic noise intruded at a size of about 0.65 μ. Apparently, a small aperture tube cannot retain the same range of coverage as a larger one—e.g., 100 μ.

**Effect of Dilution on Emulsion Stability.** The third problem is the most serious limitation on the application of the Coulter counter to sizing O/W emulsions since it requires that the emulsions be diluted with electrolyte solution prior to the analysis. Depending on the concentration of oil droplets, a dilution factor of over 10,000 is often required to make the dispersed oil droplets dilute enough to avoid serious coincidence loss. The dilution can then cause instability of the dispersed emulsion system (Groves, 1968). Although the Coulter counter has been widely used for studying aggregation and flocculation behavior of O/W emulsions, the effect of dilution has been largely overlooked or ignored (for instance, Rowe, 1965).

One of the few studies dealing with the dilution effect is that of Singleton and Brown (1965) who found that the number of particles in diluted intravenous fat emulsions was dependent upon the elapsed time of contact of the emulsions with the diluting saline electrolyte. The original particle numbers were then determined by extrapolation to zero time. The increase in particle numbers observed after dilution was attributed to coalescence or aggregation of particles smaller than the sizing limit. This coalescence can be retarded by adding glycerin or other stabilizer to the electrolyte (Groves, 1968) but the amount of glycerin must first be determined by trial and error for each sample (Sprow, 1967). The rate of aggregation was dependent on the critical micelle concentration of surfactant in the emulsion. A loss in count with elapsed time was observed for emulsions with concentration of surfactant lower than the critical micelle concentration (Shotten and Davis, 1968).

For all the oil emulsions prepared in the present investigation a consistently large reduction in count was observed, especially in the first few minutes after dilution (Table Ia). Although the loss in count was noted by Shotten and Davis (1968), and by Loriston-Clarke and Thew (1969), a decrease of this magnitude was not reported before. The rate of loss in count after dilution was less if oil-saturated electrolyte solution was used for the dilution (Table Ib), which indicated that dissolution of the oil phase in the diluent could be the main cause of the observation. When we saturated the electrolyte solution with the oil and employed the method of zero-time extrapolation, a more accurate size distribution was obtained without employing such special techniques as polymer dispersion (Rehfeld, 1967). Results of this analysis method are presented.

## *Experimental*

**Preparation of Emulsions.** Tetralin of chemical reagent grade was chosen as the dispersed oil phase because its density is close to that of water and thereby the sedimentation of oil droplets during the sizing could be eliminated. A wide range of O/W ratios and surfactant concentrations has been studied but, for the purpose of this discussion, only one emulsion is described here. The emulsion consisted of 20 ml tetralin and 180 ml filtered water containing 1.11% by weight of Tween 80 so that the final emulsion contained 1% by weight of the surfactant. The mixture was emulsified with a Virtis homogenizer model 25 at a speed of 10,000 ± 1000 rpm for 10 min.

**Electrolyte Solutions.** A saline solution with 3% sodium chloride was filtered three times through 0.3 μ Millipore filter membranes. The solution was then shaken with filtered tetralin and left to separate overnight. This solution was then saturated with tetralin. The unsaturated

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**Tables Ia and Ib. Particle Size Distribution of 10% Tetralin/Water Emulsion**

Dilution factor = $1.27 \times 10^4$. Volume of sample sized = 0.05 ml

Ia. The diluent was not saturated with tetralin

Ib. The diluent was saturated with tetralin

| Coulter counter channel no. | Particle diam, μ no. of particles counted | Table Ia. Elapsed time, sec | | | | | | | Table Ib. Elapsed time, sec | | | | | | Zero time |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 30 | 60 | 90 | 120 | 150 | 180 | 600 | 30 | 60 | 90 | 120 | 150 | 180 | |
| 14[a] | 0.50–0.75 | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... |
| 13 | 0.75–1.0 | 1809 | 1926 | 2482 | 2848 | 2614 | 2354 | 1800 | 4012 | 2847 | 2637 | 2243 | 2294 | 2386 | 6000 |
| 12 | 1.0–1.5 | 3680 | 1518 | 1012 | 732 | 761 | 780 | 430 | 6917 | 4760 | 3495 | 2661 | 2314 | 1842 | 10000 |
| 11 | 1.5–2.0 | 2969 | 1428 | 675 | 339 | 184 | 163 | 50 | 5739 | 3897 | 2858 | 2292 | 1709 | 1415 | 7500 |
| 10 | 2.0–2.5 | 2222 | 969 | 469 | 321 | 132 | 102 | 11 | 4021 | 2806 | 2170 | 1651 | 1280 | 1035 | 6000 |
| 9 | 2.5–3 | 1254 | 588 | 263 | 182 | 85 | 59 | 1 | 2134 | 1524 | 1196 | 917 | 737 | 564 | 3000 |
| 8 | 3–4 | 1503 | 796 | 355 | 237 | 136 | 94 | 5 | 2647 | 1976 | 1501 | 1168 | 964 | 801 | 3700 |
| 7 | 4–5 | 377 | 217 | 131 | 84 | 51 | 45 | 2 | 671 | 487 | 390 | 355 | 314 | 245 | 900 |
| 6 | 5–6 | 108 | 73 | 46 | 37 | 28 | 46 | 0 | 199 | 184 | 147 | 115 | 94 | 101 | 260 |
| 5 | 6–7 | 39 | 21 | 15 | 23 | 10 | 19 | 0 | 72 | 57 | 49 | 49 | 41 | 33 | 90 |
| 4 | 7–8 | 12 | 6 | 8 | 5 | 4 | 8 | 0 | 23 | 19 | 24 | 12 | 22 | 13 | 28 |
| 3 | 8–9 | 8 | 5 | 2 | 4 | 3 | 5 | 1 | 9 | 12 | 4 | 5 | 6 | 7 | 9 |
| 2 | 9–10 | 4 | 1 | 2 | 1 | 1 | 7 | 0 | 6 | 0 | 2 | 3 | 3 | 1 | 4 |
| 1 | 10–12.5 | 3 | 2 | 0 | 0 | 5 | 5 | 0 | 2 | 2 | 1 | 1 | 0 | 1 | 2 |
| 0 | 12.5– | 1 | 1 | 1 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |

[a] The counts in channel 14 are ignored because of the large background noise.

and the saturated electrolytes were used as indicated in Tables Ia and Ib. All glassware used was rinsed with the appropriate electrolyte. Correction for background count was not necessary for particle sizes larger than 1.50 μ and was not more than 10% for the size range 0.75–1.0 μ. The temperature at which the solution and the emulsion were stored was 70°F.

**Counter.** The particle size analyses were obtained by a Coulter counter model T with an adjustable threshold unit employing a 30-μ aperture tube calibrated with standard latex particles of 2.02 and 3.49 μ. The advantage in using the model T is that it can produce a complete particle size distribution in 15 increments (channels) in a few seconds whereas the model B requires manual adjustment of channels, one at a time, over many minutes.

**Procedure for Particle Counting.** The adjustable threshold unit was set as shown in Tables Ia and Ib to cover the whole aperture range. The emulsion was diluted twice before the analysis. Exactly 1 ml of the emulsion was first diluted with 100 ml of the electrolyte solution; then 1, 2, or 3 ml of this first dilution was again diluted with 250 ml of the electrolyte solution in a sample beaker for analysis. For convenience, these final solutions are designated as A, B, and C, respectively. The elapsed time after the second dilution was noted. The first count was made at an elapsed time of 30 sec to ensure that the oil droplets were uniformly dispersed. Generally a 30-sec interval was kept between the countings. The time for each counting was set at 14 sec, which represented a volume of 0.05 ml diluted emulsion. At all times, the diluted emulsion was gently stirred.

### *Results and Discussion*

Typical results of the counting of particle numbers for the diluted emulsion B as described above at a series of elapsed times are given in Table Ib. For comparative purposes, results from an identical experiment performed using diluting electrolyte not previously saturated with tetralin are presented in Table Ia. The decrease in numbers in most size ranges in Table Ia is so great that the original size distribution cannot accurately be reconstructed.

When we use Table Ib, the correct count at zero time can be obtained by extrapolating the plot of particle number against elapsed time. These results indicate that the loss in count for oil droplets less than 3 μ in diameter amounted to about 50% in the first minute, and that the percentage loss is inversely related to the particle diameter. The dependence of the particle number on the elapsed time is better illustrated in Figure 1 in which the cumulative particle numbers are plotted against the particle diameter. The solid curve represents the cumulative particle number at zero time. Particles larger than 7 μ in diameter were small in number so that fluctuation in the count was expected; nevertheless, it appears that a slight loss in number with respect to the elapsed time occurred.

To examine dilution changes quantitatively, the emulsion was diluted to various extents. The results are plotted in Figure 2 for the diluted emulsion solutions A, B, and C as described above, and show that the cumulative particle numbers of B or C were about twice or three times that of A at a particular particle diameter as expected.

The correct size distribution in the present investigation, then, could only be established if the electrolyte solution was saturated with oil and if the method of zero-time extrapolation was employed. This is apparently due to the dissolution of the oil droplets into the electrolyte solution as indicated before. If we take the diluted emulsion B, for example, the total volume of all oil particles amounted to only $1.98 \times 10^{-3}$ ml. However, using the correlation of Leinonen et al. (1971), the estimated solubility of tetralin in water at 25°C and atmospheric pressure is about 100 ppm, which is close to the measured values for many hydrocarbons. Thus the amount of oil required to saturate 250 ml of the electrolyte solution in the final dilution is about $2.5 \times 10^{-2}$ ml which is 16 times more than the amount of oil phase present in emulsion B.

To examine the dissolution process further, it is of interest to estimate the dissolution rate of the suspended oil particles. The first problem, of course, is to determine the mass transfer coefficient, $k$, of the oil from the particle surface to the continuous phase. Since the system was constantly under slow stirring during the counting, the value of the Sherwood number ($N_{Sh} = kd/D$, where $d$ is particle diameter and $D$ is the diffusivity) was expected to be greater than the limiting value two for a spherical particle when the Reynolds number approaches zero ($N_{Re} \rightarrow 0$) (Grassman, 1971). Since there exists no rigorous correlation for calculating $N_{Sh}$, the following two correlations were used (Grassman, 1971; Treybal, 1963):

$$N_{Sh} = 2.0 + 0.6 N_{Re}^{1/2} N_{Sc}^{1/3} \tag{1}$$

$$N_{Sh} = 2.0 + 0.6(N_{Gr}N_{Sc})^{1/4} + 0.347(N_{Re}N_{Sc}^{1/2})^{0.62} \tag{2}$$

If the oil particles are assumed to be spherical, and if the relative velocity of oil particles with respect to the continuous phase is 1 cm/sec, then for an oil particle of 2.5 $\mu$m in diameter (which was the mean diameter for the original particle distribution as given in Table Ib), the first correlation (Equation 1) gives $N_{Sh} = 3.3$, whereas the second correlation (Equation 2) gives $N_{Sh} = 2.4$. Accordingly, the mass transfer coefficients were estimated to be 0.051 and 0.037 g-mol/(sec) (cm$^2$) (g-mol/cm$^3$), and the initial dissolution rate to be $1.0 \times 10^{-2}$ and $0.75 \times 10^{-12}$ g/sec, respectively. The mass of a 2-$\mu$m diameter oil particle is $8.0 \times 10^{-12}$ gram. Thus, the particle would dissolve into the continuous phase completely in about 10 sec, since the dissolution rate would increase as the particle diameter decreases.

However, the data show that about 58% by weight of initial oil particles, or about 63% by number (which was about the percentage of initial oil particles less than 2 $\mu$m in diameter) were dissolved into the water after 30 sec (Table Ia).

A difference of this magnitude between the calculated and the measured values could be due to any of the following four items:

The concentration of oil in the aqueous phase is greater than zero and increases during the dissolution.

The surface of the oil particles may be somewhat protected by the surfactant which would considerably decrease the dissolution rate.

The diluted emulsion itself contains a swarm of particles which would decrease the dissolution rate compared to the calculated value based on a free particle suspended in the aqueous phase.

The estimate of particle-liquid relative velocity (1 cm/sec) may be in error.

It is, therefore, not surprising that the dilution of the oil droplets with the electrolyte solution resulted in a drastic change in number with respect to elapsed time, especially for particles in the submicron range. Hence, presaturation of the electrolyte solution with oil and use of the zero-time extrapolation is of prime importance.

It may seem puzzling that a loss in count was always observed in the present investigation even though the electrolyte was saturated with tetralin. A microscopic examination did not reveal any evidence of deaggregation, and the sedimentation effect during the counting was minimized by constant stirring. Evaporation may be a minor factor. The effect of the Kelvin equation (Davies and Rideal, 1963) for submicron particles is insignificant. A possible explanation is that the electrolyte solution was not fully saturated with tetralin because of the method of preparation. If the electrolyte solution were only 10% un-

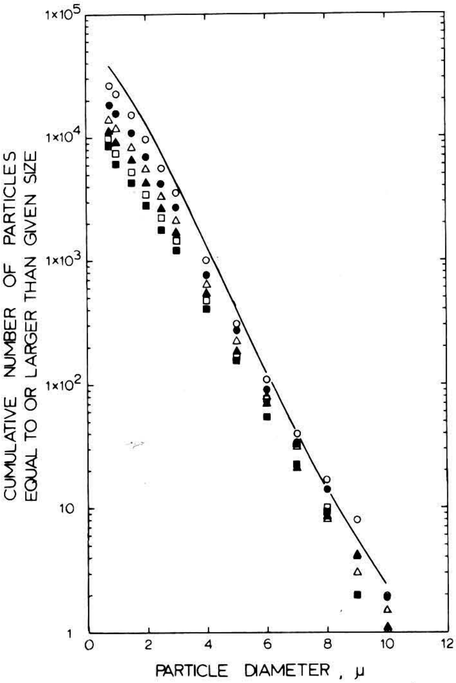

**Figure 1.** Dependence of measured particle size distributions of 10% tetralin/water emulsion on the elapsed time after dilution with tetralin-saturated electrolyte. Dilution ratio = 1.27 × 10$^4$

○ 30 sec ▲ 120 sec
● 60 sec □ 150 sec
△ 90 sec ■ 180 sec
—— zero-time extrapolation

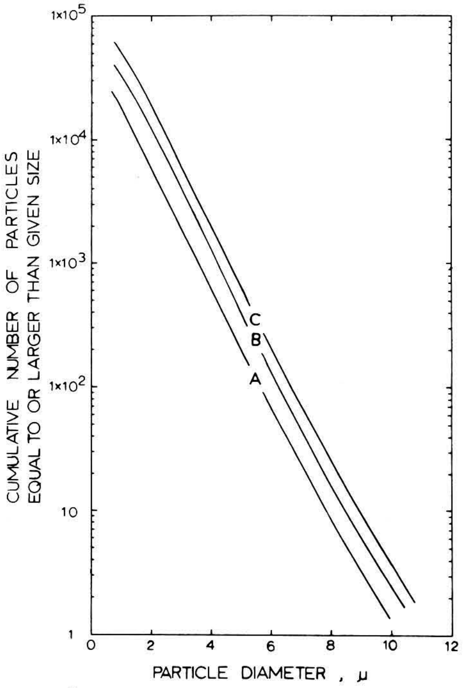

**Figure 2.** Correct particle size distributions of 10% tetralin/water emulsion at different dilution ratios. Diluent, tetralin-saturated electrolyte

| Curve | Dilution ratio |
|---|---|
| A | 2.54 × 10$^4$ |
| B | 1.27 × 10$^4$ |
| C | 0.85 × 10$^4$ |

dersaturated with the oil, the dispersed oil particles would dissolve into the solution.

The emulsion after the first dilution was very stable. Repeat measurements using this emulsion for second dilutions over a period of 2 hr showed excellent reproducibility with fluctuations of less than 5% in count. This can be explained from considerations of solubility, since the first dilution contained a total of 0.1 ml of oil and it took only about 0.01 ml of oil to saturate this 100-ml electrolyte solution.

A comparison of the total volume of oil particles counted with the original volume of the oil phase should provide a good check on the analysis. If a geometric mean diameter can be assumed for each size range as shown in Table Ib, a total volume of $2.7 \times 10^{-7}$ ml is obtained for 0.05 ml diluted emulsion B sized. This accounts for about 70% of the original volume of $3.9 \times 10^{-7}$ ml oil used to make up the emulsion. Higuchi et al. (1962) examined a relatively monodispersed emulsion and obtained not better than 50% of the oil phase. The missing volume of the oil phase may be due to incomplete sizing, evaporation, or the emulsification technique.

### *Conclusions*

Coulter counting is an extremely valuable method for determining particle size distributions of O/W emulsions, but care should be taken in its use. The Coulter orifice assembly should be shielded, especially when sizing particles in the submicron range. In addition, the dilution effect should be carefully examined. A correct count of particle numbers can be deduced if the diluting electrolyte solution is saturated with oil and the method of zero-time extrapolation is employed.

### *Acknowledgment*

Thanks are due to J. Schmidt and J. Diodati of Coulter Electronics for their helpful discussions.

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# Potential Effects of Thermal Discharges on Aquatic Systems

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■ Ecological changes in the aquatic environment caused by temperature increase are estimated in order to aid the decision process in siting cooling water discharges. Principal consideration is given to the fish community for which predictions of change in composition are based on lethal and preferred temperature. Six representative river systems in the country are considered. Insufficient data precluded similar community response estimations for freshwater invertebrates. However, data indicate that adequate protection of fish species results in like protection of the invertebrate fauna and thus the estimated effect of elevated temperature on freshwater fish communities will suffice as a guideline for both the protection of fish and invertebrates. Similar predictions were not possible for the marine community since thermal requirements are known for only a few species. However existing data and site studies are summarized for use as guidelines.

In response to the predicted increase in use of natural waters for cooling purposes, several comprehensive literature reviews have been compiled to provide quick reference to effects of changes in water temperature upon aquatic organisms (Brett, 1956; Wurtz and Renn, 1965; Altman and Dittmer, 1966; Welch and Wojtalik, 1968; Jensen et al., 1969; Parker and Krenkel, 1969; deSylva, 1969; Hawkes, 1969; Coutant, 1968b, 1969, 1970, 1971; Marble and Mowell, 1971). Despite this concentration of literature there has been a great reluctance by biologists to estimate the response of an aquatic system to increased water temperatures. One reason, and perhaps the basic one, is that many of the multitude of interactions within an aquatic community are unknown and the understanding of the known is hazy at best. Thus, it may seem unrealistic to predict the consequences of altering one basic environmental parameter.

Other reasons for reluctance stem from the fact that the great majority of the data available are from research programs investigating the effects of temperature elevation on single test organisms. There is a paucity of studies at the population or community level. Also, much of the research has been performed in laboratories, and there is hesitance to extrapolate laboratory results to field situations.

However, in planning the use of a waterway for cooling water discharge, it is essential to determine the amount of heated water that can be safely introduced or make some estimation of the consequences of altering the natural

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temperature regime. The authors recognize the immediate need for studies designed especially for the purpose of estimating the response of aquatic communities to elevated temperature, but feel in the absence of these data there is information enough, at least, to set forth guidelines and highlight possible problems that may be expected to result from increased water temperature. Even though only a first approximation, such guidelines would be useful in siting power plants if properly applied and qualified.

This manuscript has been prepared as a guide to the possible effects of increased water temperature on both freshwater and marine aquatic systems with special consideration to fish as the principal indicator organisms.

### *Freshwater Aquatic Systems*

**Freshwater Fish.** Data on the thermal requirements for 85 species of freshwater fish were tabulated by Bush et al. (1972) and have been placed with the ACS Microfilm Depository Service. Although the data are the result of numerous studies using a variety of experimental techniques, they provide a good approximation of the thermal tolerance limit and preferred temperature for a significant sample of the important fish species.

By tabulating the typical fish species inhabiting a river system and compiling the available data on thermal requirements for the species, estimations were made on which fish species would be adversely affected by in-

**Table I. Estimated Effect of Increasing Water Temperature on Fish Community of Columbia River**[a]

| °C | °F | % of species within preferred temp range | % of species in suboptimal temp conditions[b] | % of species expected to be lost from system | Species expected to be lost from system |
|---|---|---|---|---|---|
| 8 | 46.4 | 100 | 0 | 0 | |
| 10 | 50.0 | 95 | 5 | 0 | |
| 12 | 53.6 | 93 | 7 | 0 | |
| 14 | 57.2 | 88 | 12 | 0 | |
| 16 | 60.8 | 60 | 40 | 0 | |
| 18 | 64.4 | 54 | 44 | 2 | Columbia River smelt |
| 20 | 68.0 | 51 | 44 | 5 | Freshwater smelt |
| 22 | 71.6 | 28 | 65 | 7 | Puget Sound smelt |
| 24 | 75.2 | 26 | 48 | 26 | Sockeye salmon, chinook salmon, chum salmon, pink salmon, coho salmon, Dolly Varden, Rocky Mt. whitefish, chiselmouth jack |
| 26 | 78.8 | 16 | 44 | 40 | Brook trout, Aleutian sculpin, prickly sculpin, Columbia sculpin, sculpin, starry flounder |
| 28 | 82.4 | 9 | 49 | 42 | Lake trout |
| 30 | 86.0 | 9 | 26 | 65 | White sturgeon, green sturgeon, American shad, cutthroat trout, brown trout, longnose sucker, tuichub, squawfish |
| 32 | 89.6 | 7 | 12 | 81 | Rainbrow trout, coarsescale sucker, yellow perch, freshwater burbot, Columbia finescale sucker, chiselmouth, longnose dace, western speckled dace, Columbia R. chub |
| 34 | 93.2 | 0 | 14 | 86 | Redside shiner, threespine stickleback |
| 36 | 96.8 | 0 | 7 | 93 | Tadpole madtom, smallmouth bass, black crappie |
| 38 | 100.4 | 0 | 0 | 100 | Carp, largemouth bass, bluegill |

[a] Based on preferred and lethal temperature data for adult and juvenile fish. Where specific data for a species were unavailable, data from closely related species were used.

[b] Temperature range above the preferred temperature and below the lethal temperature.

**Table II. Estimated Effect of Increasing Water Temperature on Fish Community of Sacramento River**[a]

| °C | °F | % of species within preferred temp range | % of species in suboptimal temp conditions[b] | % of species expected to be lost from system | Species expected to be lost from system |
|---|---|---|---|---|---|
| 8 | 46.4 | 100 | 0 | 0 | |
| 10 | 50.0 | 97 | 3 | 0 | |
| 12 | 53.6 | 95 | 5 | 0 | |
| 14 | 57.2 | 92 | 8 | 0 | |
| 16 | 60.8 | 72 | 28 | 0 | |
| 18 | 64.4 | 72 | 28 | 0 | |
| 20 | 68.0 | 69 | 28 | 3 | Freshwater smelt |
| 22 | 71.6 | 59 | 36 | 5 | Sacramento smelt |
| 24 | 75.2 | 38 | 44 | 18 | Pink salmon, chum salmon, coho salmon, sockeye salmon, chinook salmon |
| 26 | 78.8 | 33 | 41 | 26 | Aleutian sculpin, prickly sculpin, rough sculpin |
| 28 | 82.4 | 23 | 51 | 26 | |
| 30 | 86.0 | 15 | 49 | 36 | White sturgeon, green sturgeon, brown trout, Sacramento squawfish |
| 32 | 89.6 | 8 | 46 | 46 | Rainbrow trout, California sucker, Sacramento smallscale sucker, striped bass |
| 34 | 93.2 | 0 | 33 | 67 | Hardhead, Sacramento blackfish, splittail, hitch, western roach, tuichub, thicktail chub, threespine stickleback |
| 36 | 96.8 | 0 | 13 | 87 | White catfish, channel catfish, brown bullhead, black bullhead, smallmouth bass, black crappie, Sacramento perch, green sunfish |
| 38 | 100.4 | 0 | 0 | 100 | Threadfin shad, carp, largemouth bass, spotted bass, bluegill |

[a] Based on preferred and lethal temperature data for adult and juvenile fish. Where specific data for a species were unavailable, data from closely related species were used.

[b] Temperature range above the preferred temperature and below the lethal temperature.

creased water temperature. Such estimations are presented for six representative river systems in the U.S. The estimations are based upon three assumptions: that a fish species would be lost from an area, either by death or emigration, if the water temperature was raised to the lethal limit for that species, that a fish would be subjected to suboptimal conditions that would have a detrimental effect on its activity, growth, and survival or would avoid the reach of the river if the water temperature in that reach were raised above the preferred temperature of the species, and that a change in the temperature regime that did not raise the water temperature above a fish's preferred temperature would not have an adverse effect on that species.

The estimated community response of freshwater and anadromous fish species to elevated temperature for six representative river systems is presented in Tables I–VI. The river systems chosen were the Columbia River, Sacramento River, Upper Mississippi River, Lower Mississippi River, Tennessee River, and the Delaware River. No one reach of each river will contain all the fish species indicated for the river system. Thus, in using these tables, the reader must be aware of the fish species in the reach of the river concerned, and must adjust for fish species

**Table III. Estimated Effect of Increasing Water Temperature on Fish Community of Upper Mississippi River**[a]

| °C | °F | % of species within preferred temp range | % of species in suboptimal temp conditions[b] | % of species expected to be lost from system | Species expected to be lost from system |
|---|---|---|---|---|---|
| 18 | 64.4 | 100 | 0 | 0 | |
| 20 | 68.0 | 98 | 2 | 0 | |
| 22 | 71.6 | 75 | 25 | 0 | |
| 24 | 75.2 | 61 | 39 | 0 | |
| 26 | 78.8 | 49 | 51 | 0 | |
| 28 | 82.4 | 18 | 82 | 0 | |
| 30 | 86.0 | 14 | 79 | 7 | Shovelnose sturgeon, pallid sturgeon, lake sturgeon, emerald shiner |
| 32 | 89.6 | 7 | 49 | 44 | Blue sucker, largemouth buffalofish, smallmouth buffalofish, quillback carpsucker, rabbitmouth sucker, silver redhorse, golden redhorse, greater redhorse, blacknose dace, longnose dace, creek chub, white bass, yellow bass, yellow perch, sauger, walleye, log perch, slenderhead darter, greenside darter, Johnny darter, banded darter |
| 34 | 93.2 | 2 | 35 | 63 | Stoneroller, golden shiner, redside dace, fathead minnow, bluntnose minnow, bullhead minnow, redfin shiner, mimic shiner, blackchin shiner, ironcolor shiner, spottail shiner |
| 36 | 96.8 | 0 | 12 | 88 | Northern pike, blue catfish, channel catfish, flathead catfish, yellow bullhead, brown bullhead, black bullhead, stonecat, madtom, smallmouth bass, black crappie, white crappie, warmouth, green sunfish |
| 38 | 100.4 | 0 | 2 | 98 | Gizzard shad, carp, largemouth bass, bluegill, orange-spotted sunfish, pumpkinseed |
| 40 | 104.0 | 0 | 0 | 100 | Banded killifish |

[a] Based on preferred and lethal temperature data for adult and juvenile fish. Where specific data for a species were unavailable, data from closely related species were used.
[b] The temperature range above the preferred temperature and below the lethal temperature.

**Table IV. Estimated Effect of Increasing Water Temperature on Fish Community of Lower Mississippi River**[a]

| °C | °F | % of species within preferred temp range | % of species in suboptimal temp conditions[b] | % of species expected to be lost from system | Species expected to be lost from system |
|---|---|---|---|---|---|
| 18 | 64.4 | 100 | 0 | 0 | |
| 20 | 68.0 | 98 | 2 | 0 | |
| 22 | 71.6 | 78 | 22 | 0 | |
| 24 | 75.2 | 64 | 36 | 0 | |
| 26 | 78.8 | 50 | 50 | 0 | |
| 28 | 82.4 | 26 | 74 | 0 | |
| 30 | 86.0 | 22 | 74 | 4 | Shovelnose sturgeon, emerald shiner |
| 32 | 89.6 | 10 | 54 | 36 | River herring, blue sucker, largemouth buffalofish, smallmouth buffalofish, quillback carpsucker, carpsucker, Alabama chubsucker, rabbitmouth sucker, black redhorse, yellow bass, white bass, Arkansas sand darter, yellow perch, log perch, dusky darter, goldstripe darter |
| 34 | 93.2 | 4 | 38 | 58 | Stoneroller, golden shiner, fathead minnow, pugnose minnow, silvery minnow, cypress minnow, blacktail shiner, flagfin shiner, common shiner, blackfin shiner, river shiner |
| 36 | 96.8 | 0 | 18 | 82 | Redfin pickerel, blue catfish, channel catfish, brown bullhead, black bullhead, flathead catfish, flier, black crappie, rockbass, warmouth, green sunfish |
| 38 | 100.4 | 0 | 4 | 96 | Gizzard shad, carp, largemouth bass, spotted bass, spotted sunfish, bluegill, redear sunfish |
| 40 | 104.0 | 0 | 0 | 100 | Blackstripe topminnow, blackspotted topminnow |

[a] Based on preferred and lethal temperature data for adult and juvenile fish. Where specific data for a species were unavailable, data from closely related species were used.
[b] The temperature range above the preferred temperature and below the lethal temperature.

that are predicted to be harmed but are not present. Similarly, the user must acknowledge that species not listed in the tables may indeed occur in the reach of the river concerned and these should be considered in the estimation of community response.

The estimates in Tables I–VI are based on preferred and lethal temperature data for adult and juvenile fish. They exclude the effect of increased water temperature on spawning and egg hatching success. Where specific data for a species were not available, data from closely related species (species from the same genus or family) were used.

Referring to Tables I–VI, the first column gives 2°C (3.6°F) increases in river temperature with the succeeding four columns showing the estimated fish community response to that temperature change. The second column lists the percent of species that are within their preferred

**Table V. Estimated Effect of Increasing Water Temperature on Fish Community of Tennessee River**[a]

| °C | °F | % of species within preferred temp range | % of species in suboptimal temp conditions[b] | % of species expected to be lost from system | Species expected to be lost from system |
|---|---|---|---|---|---|
| 12 | 53.6 | 100 | 0 | 0 | |
| 14 | 57.2 | 99 | 1 | 0 | |
| 16 | 60.8 | 99 | 1 | 0 | |
| 18 | 64.4 | 97 | 3 | 0 | |
| 20 | 68.0 | 96 | 4 | 0 | |
| 22 | 71.6 | 72 | 28 | 0 | |
| 24 | 75.2 | 61 | 39 | 0 | |
| 26 | 78.8 | 51 | 48 | 1 | Brook trout |
| 28 | 82.4 | 21 | 78 | 1 | |
| 30 | 86.0 | 15 | 81 | 4 | Shovelnose sturgeon, brown trout |
| 32 | 89.6 | 6 | 43 | 51 | Skipjack herring, rainbrow trout, blue sucker, smallmouth buffalofish, largemouth buffalofish, highfin carpsucker, carpsucker, spotted sucker, hogsucker, silver redhorse, shorthead redhorse, river redhorse, black redhorse, golden redhorse, white sucker, longnose dace, white bass, walleye, sauger, log perch, gilt darter, dusky darter, speck darter, greenside darter, Tennessee snubnose darter, Johnny darter, goldstripe darter, banded darter, redline darter, spottail darter, Cumberland fantail darter |
| 34 | 93.2 | 1 | 30 | 69 | Stoneroller, golden shiner, bluntnose minnow, river chub, blotched chub, spotfin chub, bigeye chub, common shiner, popeye shiner, mimic shiner, Tennessee shiner, silver shiner |
| 36 | 96.8 | 0 | 12 | 88 | Muskellunge, blue catfish, channel catfish, flathead catfish, brown bullhead, stonecat, smallmouth bass, black crappie, white crappie, warmouth, longear sunfish, orangespotted sunfish, redear sunfish |
| 38 | 100.4 | 0 | 1 | 99 | Gizzard shad, threadfin shad, carp, largemouth mass, spotted bass, rockbass, bluegill |
| 40 | 104.0 | 0 | 0 | 100 | White streaked killifish |

[a] Based on preferred and lethal temperature data for adult and juvenile fish. Where specific data for a species were unavailable, data from closely related species were used.
[b] Temperature range above the preferred temperature and below the lethal temperature.

**Table VI. Estimated Effect of Increasing Water Temperature on Fish Community of Delaware River**[a]

| °C | °F | % of species within preferred temp range | % of species in suboptimal temp conditions[b] | % of species expected to be lost from system | Species expected to be lost from system |
|---|---|---|---|---|---|
| 12 | 53.6 | 100 | 0 | 0 | |
| 14 | 57.2 | 100 | 0 | 0 | |
| 16 | 60.8 | 100 | 0 | 0 | |
| 18 | 64.4 | 96 | 4 | 0 | |
| 20 | 68.0 | 82 | 18 | 0 | |
| 22 | 71.6 | 72 | 28 | 0 | |
| 24 | 75.2 | 52 | 48 | 0 | |
| 26 | 78.8 | 36 | 62 | 0 | Smelt |
| 28 | 82.4 | 26 | 70 | 4 | Alewife |
| 30 | 86.0 | 20 | 66 | 14 | Tomcod, Atlantic sturgeon, shortnose sturgeon, American shad, Atlantic salmon |
| 32 | 89.6 | 8 | 24 | 22 | Alewife, hickory shad, common sucker, spotted sucker, chubsucker, eastern redhorse, hogsucker, blacknose dace, pearl dace, silverline shiner, striped bass, white perch, yellow perch, blackside darter, Johnny darter, creek chub |
| 34 | 93.2 | 2 | 32 | 66 | Fallfish, golden shiner, fathead minnow, bluntnose minnow, northern chub, satinfin shiner, bridled shiner, swallowtail shiner, silvery minnow, silverfin shiner, threespine stickleback |
| 36 | 96.8 | 0 | 12 | 88 | Chain pickerel, redfin pickerel, white catfish, yellow bullhead, brown bullhead, madtom, banded sunfish, bluespotted sunfish, rockbass, yellowbelly sunfish, smallmouth bass |
| 38 | 100.4 | 0 | 2 | 98 | Gizzard shad, carp, largemouth bass, bluegill, pumpkinseed |
| 40 | 104.0 | 0 | 0 | 100 | Variegated cyprinodon |

[a] Based on preferred and lethal temperature data for adult and juvenile fish. Where specific data for a species were unavailable, data from closely related species were used.
[b] The temperature range above the preferred temperature and below the lethal temperature.

temperature range at the given temperature. A fish species is assumed to be within this range if the given water temperature (or mixed river temperature) is lower than the highest reported preferred temperature determined at the highest acclimation temperature for the fish.

The preferred temperature is indicative of the most favorable temperature for a fish and to a large extent determines the fish's distribution (Sullivan, 1954). If a fish is subjected to a temperature above its preferred temperature, there will probably be an avoidance reaction. If the fish remains in the area, all its life processes will be adversely affected and it will function at reduced efficiency depending on the extent of the temperature increase above the preferred level.

The third column in the tables lists the percent of species able to survive in the area but at suboptimal temperature conditions. This is the sublethal temperature range above which a fish prefers but below its lethal limit. In this temperature range, the fish is considered stressed and an adverse effect on its activity, growth, and survival is predicted. Exposures to sublethal temperatures over long periods of time can be just as harmful as lethal temperatures and may cause the elimination or drastic reduction in the population size of stressed species even to the eventual elimination of species (Tarzwell, 1970).

The last two columns (four and five) in the tables give the percent of species and their identification that is expected to be lost from the reach of the river heated to the water temperature given in the first column. Except for the anadromous fish, the temperature at which a species is expected to be lost from the system was derived from the highest recorded lethal limit reported in the literature unless it seemed atypical as compared to the other limits reported. Although numerous factors such as season, sex, age, physiological condition, water chemistry and acclimation cause variation in the experimentally determined lethal limit, the use of the highest reported lethal temperature can safely be assumed to reduce significantly the survival or occurrence of the fish in question in the reach of river affected. Because of the possibility of these estimates being too liberal (i.e., fish will be killed or emigrate at lower temperatures), importance of the fraction of fish in suboptimal conditions surely should not be overlooked for it may be a better guide for siting thermal discharges. If the only reported lethal limits for a fish were determined at low acclimation temperatures, the estimation of lethal limits at a higher acclimation temperature was derived from proportions developed from data with closely related species. During their migration through a reach of a river with elevated temperatures, anadromous fish would not have time for full acclimation to the heated waters. Therefore the temperature at which an anadromous fish was estimated to be lost from the system was derived from lethal limits determined at intermediate acclimation temperatures.

In most cases the lethal limits reported in the literature were presented as the TLm (median tolerance limit) or LD-50 (lethal dose—50%). Such data indicate that 50% of the fish suffered mortality at the indicated temperature and exposure time (usually four days). According to Mihursky (1969), short-term lethal tests have indicated that only a 0.5°C (1°F) to a little over 1°C (2°F) increase in temperature may be the difference between a low percentage mortality and 100% mortality. Likewise Brett (1960) indicated that the difference between temperatures that produce 5 and 50% lethality is small, suggesting a large increase in mortality can result from a small change in temperature near the tolerance limit. The use of the highest reported lethal limit for prediction of the loss of a fish species from a reach of a river sustaining the given temperature would certainly be a liberal estimate of the effect—that is, loss is possible at a lower temperature but highly probable at the given temperature.

The tables of estimates of alterations in fish communities in a river are meant to set forth guidelines and highlight possible problems that are expected to result from increased water temperature. The accuracy of these estimates must be qualified not only because of the varied techniques used by researchers who produced the data upon which the predictions are based, but also because they do not consider the response of a fish species to the numerous other environmental variables that interact with a temperature increase to affect the species. These altered responses would result from, for example, changes in dissolved oxygen, synergism of increased temperature and toxins, susceptibility to disease and parasites, loss or gain of competitive advantage, and influences on a fish's food, shelter, and predators.

It is impossible at this time to integrate all the biotic and abiotic environmental variables that change with increased water temperature into a comprehensive table to predict effects on fish. If possible, such integration would undoubtedly indicate a loss of more native fish species from a river system than would result from consideration of temperature alone. In this sense the estimates in the tables are probably again liberal. Recognizing the need for such qualification and more detailed studies at most sites, we think these estimates will be useful as guidelines in predicting the consequences from altering the natural temperature regime in a section of a river. Of particular importance will be the table column listing the percent of species in suboptimal conditions. The purpose of the tables is to add the initial evaluation of thermal power plant siting and cooling water discharges. In no way do these preliminary estimates replace the need for extensive studies to define thermal environmental impacts at the selected site.

Although the six-sample environments are widely separated geographically and also probably in temperature regime, a remarkable similarity in estimated community effect is seen in five of the environments (Tables II–VI). At about 24 ± 2°C (75.2 ± 3.6°F) fewer than one half of the fish species in each of five environments, upper and lower Mississippi, Tennessee River, Delaware River, and the Sacramento River, are within their preferred temperature range. Between 32 and 34°C (89.6 and 93.2°F) is the break point where one half of the fish species are expected to be lost from the system. The maximum allowable temperature with unspecified duration is listed in many State standards for warm water streams as 90°F (32.2°C). In contrast to those five similar environments, the Columbia River contains a larger proportion of cold water forms. There (Table I) one half of the fish species would be beyond their preferred range if the temperature exceeded 20°C (68°F), while one half the species would be lost between 28 and 30°C (82.4 and 86°F). Even though similar to the warm water rivers when temperatures causing a 50% community effect are considered, the Sacramento must be considered a cold water environment like the Columbia because the temperature at which species begin to be lost is similar (18–20°C) (64.4 and 68°F).

### *Freshwater Invertebrates*

The data compiled from the literature search for lethal temperature limits for freshwater invertebrates are reported by Bush et al. (1972) and are on file with the ACS Microfilm Depository Service. The literature search indicated that temperature tolerances have been determined for only a small percent of the total number of freshwater invertebrate species. There is estimated to be about 8500 described species of freshwater invertebrates excluding protozoa and parasitic classes (Pennak, 1953). The relatively small number (94) of species for which data on thermal requirements are available precludes community response estimations similar to those given for freshwater fish. However, there seems to be evidence that in protecting fish, the invertebrate fauna will also be protected (Mount, 1969). Further there does not seem to be an example in the literature of a heated discharge destroying the bottom fauna to the extent that the fish population was adversely affected by lack of food organisms. Parker and Krenkel (1969) site Usinger as stating that the heat tolerance of most macroscopic invertebrates is well above that of fish.

If the 94 invertebrates for which data on lethal limits reported by Bush et al. (1972) (ACS Microfilm Depository Service) are representative of the tolerance range of freshwater invertebrates in general, then Figure 1 supports the thesis that protection of the fish will in general result in the protection of most invertebrate fauna or at least an adequate fish food supply. Figure 1 gives the mean lethal temperature for each freshwater fish and invertebrate, respectively, for which data were found. The figure suggests that when nearly all fish species are protected from heated water discharge the invertebrate organisms would also be protected. At least, as Mount (1969) suggested, there would be food organisms present. In an extreme case, Figure 1 indicates that invertebrate species, many of which are fish food items, will still exist after all fish are killed by heat.

Studies of the effects of raised water temperature on macroinvertebrate communities have been few. Both Trembly (1960) and Coutant (1962) reported on the effects of heated water discharge from the Martins Creek power plant on the benthic organisms of the Delaware River. Each showed a reduction in the number and diversity of benthic organisms in the zone receiving heated water. Normal abundance and diversity were established about a mile downstream from the discharge. A tolerance limit near 32.2°C (90°F) was suggested for a normal community composition. At temperatures above 32.2°C (90°F) a substantial loss in numbers, diversity and biomass occurred.

In agreement with Trembly's results, Strangenbery and Pawlaczyk (1962) reported that bottom organisms decreased in numbers when a river receiving a heated water discharge exceeded 30°C (86°F). Also Wurtz (1970) reported on a study where 35°C (95°F) was commonly exceeded below a power plant discharge in a Pennsylvania stream. However, the results indicated a less severe reduction in species than would be expected if 32°C (89.6°F) were the upper tolerance limit for the bottom organisms [as found by Trembly (1960) for the Delaware River].

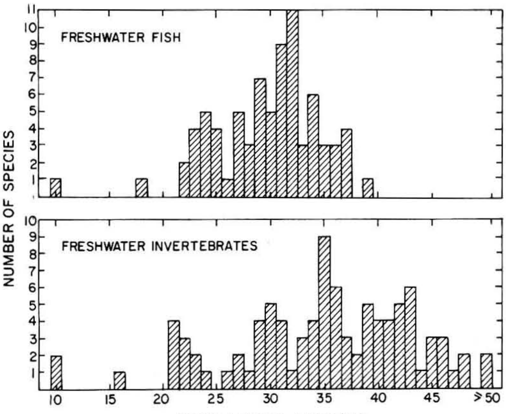

Figure 1. Number of species and mean lethal limit for freshwater fish and invertebrates

Because of the regional variation in the composition of invertebrate fauna, results from the few studies reported above may not be indicative of the temperature tolerance for an invertebrate community in general and therefore are not a sound basis for guidelines. However, if indeed the adequate protection of fish species results in like protection of the principal invertebrate fauna, at least to the extent that there will be preservation of fish food organisms to support the fish population, then the use of the tables on the estimated effect of elevated temperature on freshwater fish communities will suffice as a guideline for both the protection of fish and invertebrates.

**Freshwater Algae.** The composition of an algal community in a river may change with variations in environmental conditions as the competitive advantage of some forms is changed. Because of the acute competition among algal species for space, nitrients, light, etc., conditions need not reach the lethal limit for an algal species to be replaced (out-competed) by a more tolerant form. The conditions need only be unfavorable for that species and not for another. Thus, in evaluating the effect of temperature on an algal community the optimum temperature for the species is of prime concern. Differences in temperature optimums are among the major factors causing succession and dominance in algal communities.

In general, the optimum temperature for growth of diatoms is from 15–25°C (59–77°F), that for green algae 25–35°C (77–95°F) and for blue-green algae 30–40°C (86–104°F) (Hawkes, 1969) and is supported by data compiled by Bush et al. (1972) (ACS Microfilm Depository Service). Whether increased water temperature would result in succession to the more tolerant forms would depend on other environmental conditions such as light and nutrient supply. However if light and nutrients are sufficient, and the temperature change is great enough, succession in algal composition from diatoms to a flora predominantly of green algae or blue-green algae will occur. The determining factor then is whether the change in temperature is "great enough" and the duration long enough.

Patrick et al. (1969) were able to induce succession to a blue-green flora from a diatom flora in study streams by increasing the water temperature above 35°C (95°F). In concluding a presentation on temperature effects on freshwater algae, Patrick (1969) stated that blue-green algae will often become dominant when the water temperature is maintained above 35°C (95°F) for fairly long periods of time. If the temperature is held between 32.5 and 35°C (90.5–95°F) an increase in green algae can be expected. Below these temperatures she indicated diatoms usually dominate, assuming the streams were already populated by diatoms and were not previously affected by other pollution which had changed the flora from a community dominated by diatoms. It should be noted that the algal community of many streams is composed predominantly of blue-green algal forms while the water temperature is well below 35°C (95°F). Succession to blue-green algae can be caused by nutrient enrichment without an increase in temperature.

Studies made concerning passage of algae through a power station condenser system indicate that little if any harm will result to the algae if the temperature does not exceed 34–34.5°C (93.2–94.1°F) (Patrick, 1969). Howell (1969) reports that there was no significant damage to phytoplankton passing through the condensers of the power station at Indian Point on the Hudson River.

Morgan and Stross (1969) studied the effect of passage of algae through the condenser of an electric power generating station using algal photosynthetic rate as an indicator. Photosynthesis was stimulated by an increase of 8°C (14.4°F) when the water temperature was less than 16°C (60.8°F). An increase of 8°C (14.4°F) inhibited photosynthesis when the water temperature was greater than 20°C (68°F). In extreme cases photosynthesis was decreased by 95%. They concluded that reduction in primary production could be significant; however, a real reduction in production in receiving waters may result only if the rate of photosynthesis is herbivore controlled and not nutrient limited.

Because of the complexity and dynamics of an algal community as an integral part of an ecosystem, statements of consequences from altering the algal community structure by increased water temperature can only be speculative at best. The selection preference toward blue-green algal forms is an advancement toward dominance by nuisance algae. The community increase in blue-green algal mass is characteristically greater than the concurrent decrease of other algal forms resulting in greater total biomass (Coutant, 1966). As a result of their increased growth, the blue-green algae add to the organic enrichment of a stream. Further, the blue-green algae are not utilized in the foodweb to the extent that diatoms and green algae are. Thus, the increase production resulting from blue-green growth is lost to the higher trophic levels. The consequences of this are relatively unknown.

**Marine Fish and Invertebrates.** Data on thermal lethal limits for marine fish and invertebrates have been compiled by Bush et al. (1972) and are on file with the ACS Microfilm Depository Service. Because of the relatively small number of marine organisms for which there are available data, estimates of community response to elevated temperatures similar to those made for freshwater fish are not possible. Instead, general statements must suffice for guidelines and more emphasis must be placed on special site studies.

The thermal tolerances of the major groups of marine fish and invertebrates are summarized in Table VII in order of increasing sensitivity or decreasing tolerance. As was the case in freshwater, the most sensitive groups of organisms are the fish with mean values for thermal tolerance (lethal) limits of 26.5°C (79.7°F) and 28.3°C (82.9°F) for Osteichthyes and Chondrichthyes, respectively. Data are also most prevalent for the bony fishes. Marine phytoplankton, macroalgae, and rooted plants are not included in the table. Marble and Mowell (1971) indicate that thermal tolerance values are higher for these groups than for fish. The mean tolerance values presented by Marble and Mowell (1971) for red algae, phytoplankton, brown algae and sea grasses was 30.5°C (87°F), 32.2°C (90°F), 37.0°C (98.6°F), and 37.6°C (99.7°F), respectively.

Although studies in the vicinity of power plants are scarce, several are significant and indicate that the fish species may not be the most sensitive. The flora of Morrow Bay, Calif., was found to be much more sensitive than the fauna to heated water discharge. Abundance and species diversity of both the aquatic plants and benthic organisms were reduced for about 500 ft (152 m) from the power plant; the flora however was affected much more severely. The fish population did not seem to be affected. The mean intake temperature of the water to the power station at Morrow Bay was 13.3°C (56°F) with an annual range of 10-15.6°C (50-60°F). Temperatures 5.6°C (10°F) above normal were found within 500 ft of the discharge (Adams, 1969; Zeller and Rulifson, 1970). North and Adams (1969) suggested that if the water temperature increased 5.6°C (10°F) above summer ambient in areas on the Pacific coast, all cold water biota would be eliminated and many of the species considered to be able to tolerate warm water would be adversely affected. An increase of 1.1°C (2°F) over normal summer temperatures was predicted to reduce or eliminate cold water biota during warm summers. They report that the Laminarian kelps of California will be severely affected by a 5.6°C (10°F) increase in water temperature in the summer months and that canopy deterioration of *Macrocystis spp* (kelp) frequently occurs when summer temperatures 1.1°C (2°F) greater than normal are maintained for several weeks. Such predictions are supported by the Morrow Bay experience.

**Table VII. Thermal Tolerance of Various Groups of Marine Fish and Invertebrates**

| | Mean temp | | Range, °C | No. of species |
|---|---|---|---|---|
| | °C | °F | | |
| Order Thoracica (barnacles) | 47.3 | 117.1 | 42.3–53.7 | 5 |
| Class Xiphosura (horseshoe crabs) | 42.7 | 108.9 | 42.7 | 1 |
| Phylum Protozoa (unicellular animals) | 38.5 | 101.3 | 34 –43 | 2 |
| Phylum Mollusca (mollusks) | 37.2 | 99.0 | 29 –45.5 | 44 |
| Phylum Coelenterata (jellyfish, hydroids, sea anemones, corals) | 36.6 | 97.9 | 27.4–40.9 | 17 |
| Phylum Annelida (segmented worms) | 36.2 | 97.2 | 31.6–42.7 | 3 |
| Phylum Echinodermata (sea urchins, starfish) | 35.9 | 96.6 | 29 –40.7 | 13 |
| Phylum Arthropoda[a] (arthropods) | 34.5 | 94.1 | 17 –53.7 | 52 |
| Order Amphipoda (amphipods) | 34.4 | 93.9 | 27.5–41 | 13 |
| Order Decapoda (shrimps, lobsters, crabs) | 32.9 | 91.2 | 17 –43 | 26 |
| Phylum Ctenophora (comb jellies) | 32.1 | 89.8 | 26.5–38.2 | 4 |
| Order Eucopepoda (copepods) | 30.3 | 86.5 | 28 –32.8 | 3 |
| Order Anostraca (fairy shrimp) | 30.0 | 86.0 | 28 –42 | 2 |
| Class Chondrichthyes (fish with cartilaginous skeletons) | 28.3 | 82.9 | 26.7–29.8 | 4 |
| Class Osteichthyes (fish with at least partly ossified skeletons) | 26.5 | 79.7 | 10 –38 | 58 |
| Order Euphausiacea (euphasids) | 25.1 | 77.2 | 23.2–27 | 2 |

[a] Includes several orders and a class listed separately.

Fewer species and numbers of fish were reportedly found in the discharge area of the Turkey Point power station on Biscayne Bay, Fla. The effluent also altered the aquatic plant and benthic communities. Summer ambient temperatures were 30-31°C (86-87.8°F). Many plants and animals in the zone +4°C (7.2°F) above ambient were killed or greatly reduced. The turtle grass (*Thalassia testudium*) population was killed within the +4°C (7.2°G) isotherm. The turtle grass provided an important habitat and food source for many of the invertebrate species of the area. Within the +3°C (5.4°F) isotherm, species diversity and abundance of algae were reduced. The mollusks and crustaceans increased while the number of fish decreased in this area (Levin et al., 1972; Marble and Mowell, 1971).

A table of estimated occurrence and loss of estuarine species at various temperatures was presented by Mihursky (1969). The table was based on laboratory temperature data for 13 species (both fauna and flora) of the Chesapeake Bay system at Maryland. It was estimated that 8% of the species would be lost from the system and 61% would be in suboptimal temperature conditions at 32.2°C (90°F). At 35°C (95°F) 69% of the species were estimated to be lost from the system. Such estimates are supported by the reported effect of the heated discharge of the Turkey Point power station on Biscayne Bay, Fla.

As a guideline for the siting of cooling water discharges in the marine environment, the estimates of North and Adams (1969) for the Pacific coast and Mihursky (1969) for the Atlantic coast are the best available and are supported by site studies.

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**Supplementary Material Available.** Five tables and a reference list for the tables will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $7.00 for photocopy or $2.00 for microfiche, referring to code number *ES&T*-74-561.

# Complexation of Iron(II) by Organic Matter and Its Effect on Iron(II) Oxygenation

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■ Appreciable concentrations of dissolved ferrous iron can be maintained in aerobic aquatic systems in the presence of organic species of natural origin. Tannic acid, gallic acid, pyrogallol, and other products of natural vegetative decay can completely retard the oxidation of Fe(II) for several days, even under an oxygen partial pressure of 0.21 atm. Correspondingly, manometric measurements show that the rate of oxidation of tannic acid as reflected by the rate of oxygen consumption is inhibited in the presence of Fe(II) due to the formation of an oxidation-resistant complex between Fe(II) and tannic acid. Polarographic analyses confirm that complexation of Fe(II) by tannic acid is responsible for the inhibition of Fe(II) oxidation, the extent of complexation increasing as pH and the organic–Fe(II) ratio increase. A model is presented describing the complexation and oxidation-reduction behavior of aqueous iron in aerobic systems in the presence of organic matter.

High concentrations of iron are often associated with organic matter of natural origin in many natural aquatic systems. Previous investigators (Theis and Singer, 1973; Komolrit, 1962: Ghosh et al. 1967) have indicated that the oxidation of ferrous iron is severely retarded in many natural waters which contain humic substances, including groundwaters, surface waters, and municipal wastewaters. It has been demonstrated (Theis and Singer) that many model organic compounds which possess the structural features of humic substances are capable of significantly altering the rate of oxidation of ferrous iron from that reported by Stumm and Lee (1961) for simple aqueous media. These effects are shown in Figure 1. Gallic acid and pyrogallol completely inhibited Fe(II) oxidation, giving identical results as shown for tannic acid. Glutamic and tartaric acids behaved analogously to glutamine, while vanillic acid, vanillin, phenol, resorcinol, syringic acid, and histidine had no effect on the oxidation rate. Tannic acid was particularly effective in stabilizing high concentrations of Fe(II) for several days as illustrated in Figure 2. Furthermore, many of these same compounds were shown to rapidly reduce ferric iron as summarized in Table I.

These findings have a number of ramifications relative to water quality management. In particular, water treatment plants for the removal of iron from groundwaters rely upon the oxidation of ferrous iron by oxygen and on sedimentation and filtration of the resultant ferric hydroxide. The presence of humic substances in groundwater has been reported to interfere with iron oxidation and iron removal (Ghosh et al., 1967: Komolrit, 1962; Robinson, 1967). In addition, Davies (1970), Prakash and Rashid (1968), and Martin et al., (1971) have demonstrated that the iron associated with humic materials is generally available as a nutrient for the growth of aquatic species, and that these humic substances tend to stabilize the iron, thereby increasing its nutritive availability.

Morgan and Stumm (1964) suggested that the inhibition of Fe(II) oxidation by organic species involved the cyclic oxidation of Fe(II) followed by the reduction of Fe(III) by the organic substances. Their scheme is given in equations 1a through 1c.

$$\mathrm{Fe(II)} + \mathrm{O_2} \longrightarrow \mathrm{Fe(III)} \quad (1a)$$

$$\mathrm{Fe(III)} + \text{organic} \longrightarrow \mathrm{Fe(II)} + \text{oxidized organic} \quad (1b)$$

$$\mathrm{Fe(II)} + \mathrm{O_2} \longrightarrow \mathrm{Fe(III)} \quad (1c)$$

If the reduction step (Equation 1b) is rapid, this scheme predicts that a steady state concentration of Fe(II) will persist in the environment, even under oxidizing conditions, as long as organic matter is available to reduce

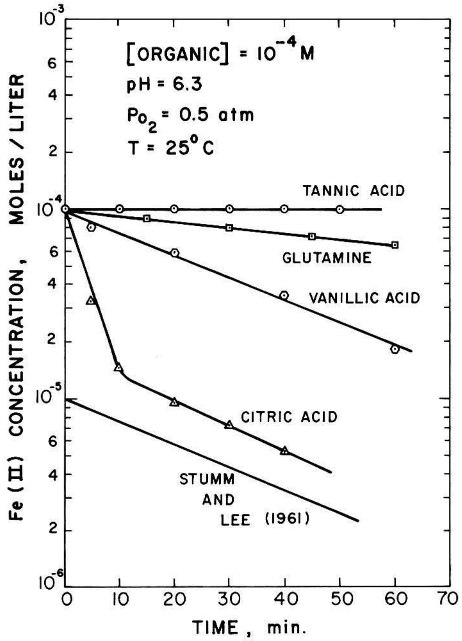

**Figure 1.** Effects of representative organic compounds on rate of oxidation of ferrous iron at pH = 6.3 $P_{O_2}$ = 0.5 atm, and $T$ = 25°C as compared with rate in simple aqueous media (Stumm and Lee, 1961) (after Theis and Singer, 1973)

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Fe(III). An interesting feature of their scheme is the implication that, in spite of the constancy of the Fe(II) concentration, oxygen is consumed and organic matter is oxidized. The Fe(II)-Fe(III) couple serves as an electron transfer catalyst in the oxidation of organic matter by oxygen.

Jobin and Ghosh (1972) provided experimental evidence for the occurrence of Equations 1a through 1c. However, their analytical technique in distinguishing between Fe(II) and Fe(III) is questionable since their samples were boiled in acid to free the iron associated with the organic matter. As Shapiro (1966) has shown, boiling drastically alters the existing ferrous-ferric ratio. Oldham and Gloyna (1969), using polarographic techniques, demonstrated that much of the iron associated with laboratory-prepared leaf leachates is in a complexed form. Schnitzer and Skinner (1964) measured stability constants for many metal humic acid complexes, including both ferrous and ferric iron. Christman (1967) emphasized the significance of chelation to explain iron-color interactions. Thus, the complexation of iron in one or both of its oxidation states may be an important additive mechanism to the scheme shown in Equations 1a through 1c.

**Table I. Reduction of Fe(III) by Model Organic Compounds**

pH = 6.3. Fe(III) added = $8.0 \times 10^{-5}M$

| Compound, $10^{-4}M$ | Quantity of Fe(III) reduced, $M$[a] |
|---|---|
| Tannic acid | $7.9 \times 10^{-5}$ |
| Pyrogallol | $6.9 \times 10^{-5}$ |
| Gallic acid | $3.4 \times 10^{-5}$ |
| Syringic acid | $2.6 \times 10^{-5}$ |
| Resorcinol | $5.2 \times 10^{-6}$ |
| Citric acid | $4.7 \times 10^{-6}$ |
| Tartaric acid | $1.9 \times 10^{-6}$ |
| Vanillic acid | $9.0 \times 10^{-7}$ |
| Vanillin | $7.0 \times 10^{-7}$ |

[a] Reduction was virtually instantaneous, as determined by analysis for change in Fe(II) concentration immediately following the addition of Fe(III) to a solution of the organic compound indicated. See Theis and Singer (1973) for analytical details.

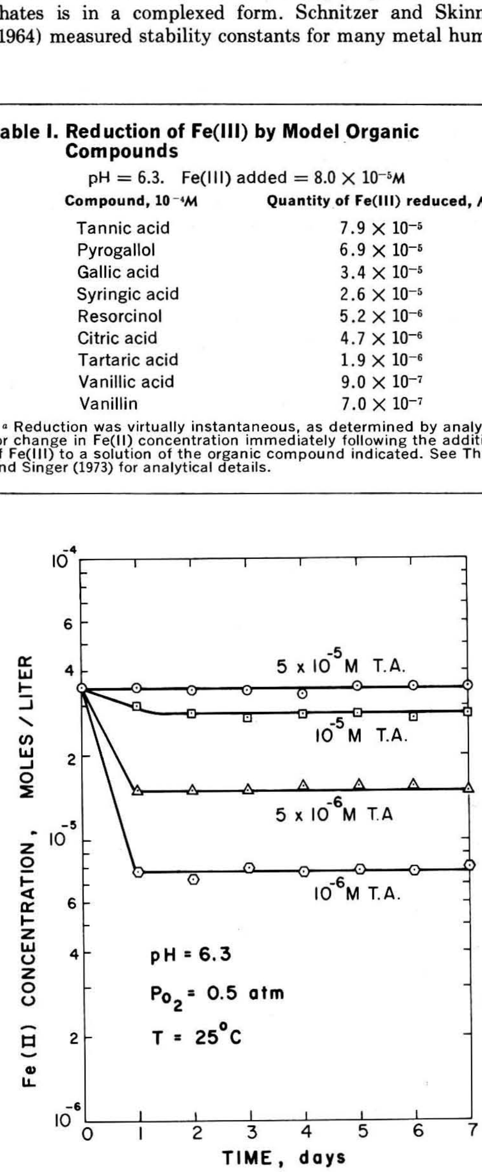

**Figure 2.** Inhibition of ferrous iron oxidation in presence of various concentrations of tannic acid, at pH = 6.3, $P_{O_2}$ = 0.5 atm, and $T$ = 25°C (after Theis and Singer, 1973)

The purpose of this investigation is to explain the mode of inhibition of Fe(II) oxidation by oxygen in the presence of dissolved organic species of humic origins, and to present a more complete picture of the behavior of iron under oxidizing conditions in natural waters.

### *Experimental*

The consumption of oxygen by a mixture of tannic acid and ferrous iron and by tannic acid alone was measured manometrically using a Warburg respirometer (Precision Scientific Co.). Equimolar concentrations of tannic acid and ferrous perchlorate were added to the reaction vessel and the pH was adjusted with concentrated $HClO_4$ or NaOH to pH values of 7.0, 9.5, and 10.8. Studies were conducted for several days, and the pH, once adjusted, exhibited little variance with time. Ferrous iron was monitored during these tests using a modification of the bathophenanthroline procedure of Lee and Stumm (1960). Aliquots were acidified initially to pH 4.5 with an acetate buffer in order to free the Fe(II) from the tannic acid and yet prevent alteration of the ferric-ferrous ratio. Boiling of samples and acidification to extremely low pH's were avoided as these steps are known to hasten the reduction of Fe(III). Microbial influences were absent; there were no differences in the results between runs previously sterilized by autoclaving and those which were not. A thermobarometer was used to account for natural fluctuations in atmospheric pressure.

Classical polarography by means of a dropping mercury electrode (DME) was employed (using a Heath Polarograph Model EUA-19-2) to distinguish free from complexed ferrous iron in the presence of tannic acid. All tests were performed under a nitrogen atmosphere to prevent oxidation of Fe(II) as well as to eliminate the oxygen knee which occurs at a potential of approximately 0.0 V. Ferrous iron is reversibly reduced at the DME and produces a clear half-wave in a 1*M* KCl supporting medium at $E_{1/2} = -1.35$ V (Meites, 1955). A standardization curve relating the diffusion current at this half-wave potential to the concentration of free ferrous iron in 1*M* KCl was linear. Various references (Milner, 1957; Kolthoff and Lingane, 1946) tend to indicate that tannic acid is not adsorbed at the Hg electrode; polarograms run on solutions of tannic acid in the absence of iron failed to detect any current potential waves in the range +0.10 to −2.0 V. Tests were performed at pH 5, 6, and 7 at various Fe(II)-tannic acid ratios. Polarographic studies utilizing solutions of ferric iron and tannic acid were also performed in an attempt to determine the relative proportion of Fe(III) reduced and complexed by tannic acid.

### *Results and Discussion*

The consumption of oxygen in systems containing ferrous iron and tannic acid, and tannic acid alone, at pH 7.0 and 10.8, is shown in Figure 3. In the absence of organic matter, the half-time for Fe(II) oxidation at pH 7.0 is 4 min (Stumm and Lee, 1961), implying complete (>99%) oxidation of Fe(II) in a relatively short time. Consequently $2.5 \times 10^{-4}$ mol/l. of $O_2$ should be consumed within a few minutes in oxidizing $10^{-3}M$ Fe(II) in accordance with the stoichiometry,

$$4Fe^{+2} + O_2 + 4H^+ = 4Fe^{+3} + 2H_2O$$

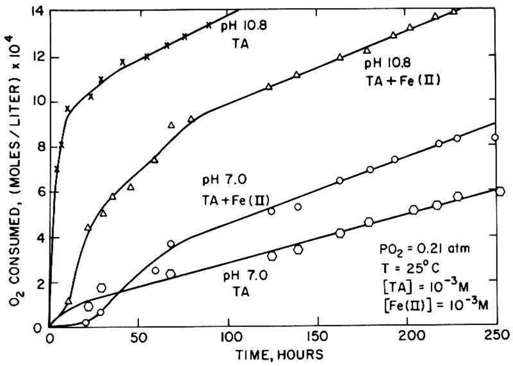

**Figure 3.** Rate of oxygen consumption by equimolar concentrations of Fe(II) and tannic acid as compared with tannic acid alone at pH 7 and 10.8, $P_{O_2}$ = 0.21 atm, and $T$ = 25°C

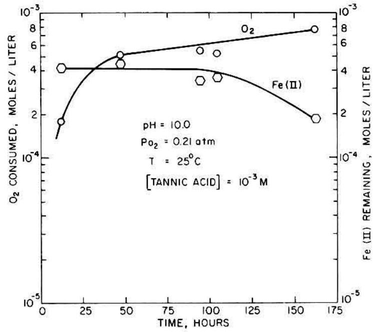

**Figure 4.** Consumption of oxygen by system of ferrous iron and tannic acid as compared with residual Fe(II) in system at pH = 10.0, $P_{O_2}$ = 0.21 atm, $T$ = 25°C, [Tannic Acid] = $10^{-3}M$

It is apparent from Figure 3 that the rate of oxygen consumption by the Fe(II)-tannic acid system at pH 7.0 is appreciably slower than the rate in the absence of organic material, again demonstrating the inhibitory effect of tannic acid on Fe(II) oxidation. Additionally, it is apparent from Figure 3 that the consumption of oxygen by tannic acid at pH 7.0 is initially inhibited in the presence of Fe(II), whereas no inhibition occurs in its absence. Following this initial lag period, the rate of oxygen consumption reflects the oxidation of both tannic acid and Fe(II). The difference between the oxygen taken up by tannic acid at pH 7.0 in the presence and absence of Fe(II) after about 100 hr is seen in Figure 3 to be approximately 2.5 × $10^{-4}$ mol/l., the equivalent amount required for the oxidation of $10^{-3}M$ Fe(II). This lag is attributed to complexation of the tannic acid by Fe(II). Furthermore, at pH 9.5 and 10.8, the presence of Fe(II) was observed to retard the oxidation of tannic acid, as illustrated for pH 10.8 in Figure 3. The rate of tannic acid oxidation by oxygen increases with pH but complexation of tannic acid by Fe(II) decreases the oxygen uptake rate at these elevated pH values.

Qualitatively, it was observed that, upon mixing the Fe(II) and tannic acid, a deep purple color resulted. At pH 10.8 this purple color of the Fe(II)-tannate complex gradually gave way to an orange suspension and, at the completion of the study, a reddish orange precipitate of ferric hydroxide had deposited in the reaction vessel. Complexation was no longer in effect and Fe(II) had undergone oxidation. This qualitative observation is supported by the quantitative results indicated in Figure 4 which shows the corresponding concentration of Fe(II) during the course of the oxygen uptake study. A steady state concentration of Fe(II) persists in the system for about 100 hr during which tannic acid undergoes oxidation as reflected by the consumption of oxygen. After about 100 hr Fe(II) oxidation begins leading eventually to Fe(III) deposition. These observations point to the formation of a stable complex between Fe(II) and tannic acid which is more resistant to oxidation at physiological pH's than either Fe(II) or tannic acid alone.

The results of the polarographic studies of ferrous iron and tannic acid substantiate this supposition and are summarized in Table II. The results indicate that as the tannic acid to ferrous iron ratio increases, the diffusion current (proportional to free aqueous ferrous iron, $Fe^{+2}$) decreases, implying a greater degree of Fe(II) complexation by tannic acid. Furthermore, as the pH increases, the diffusion current for an equivalent amount of iron and tannic acid decreases, again implying an increase in the extent of complexation with increasing pH.

**Table II. Polarographic Results for Ferrous Iron and Tannic Acid in 1*M* KCl**

| pH | Fe(II), *M*/1 | Tannic acid, *M*/1 | Diffusion current, μamp | $Fe^{+2}$, *M*/1 |
|---|---|---|---|---|
| 5.0 | $5.0 \times 10^{-4}$ | 0.0 | 4.6 | $5.0 \times 10^{-4}$ |
| | | $1 \times 10^{-4}$ | 4.6 | $5.0 \times 10^{-4}$ |
| | | $5 \times 10^{-4}$ | 3.5 | $3.8 \times 10^{-4}$ |
| | | $1 \times 10^{-3}$ | 3.0 | $3.2 \times 10^{-4}$ |
| 6.0 | $5.0 \times 10^{-4}$ | 0.0 | 4.6 | $5.0 \times 10^{-4}$ |
| | | $1 \times 10^{-4}$ | 4.2 | $4.5 \times 10^{-4}$ |
| | | $5 \times 10^{-4}$ | 1.5 | $1.6 \times 10^{-4}$ |
| | | $1 \times 10^{-3}$ | 0 | 0 |
| 7.0 | $5.0 \times 10^{-4}$ | 0.0 | 4.6 | $5.0 \times 10^{-4}$ |
| | | $5 \times 10^{-4}$ | 1.1 | $1.2 \times 10^{-4}$ |

The difference between the total ferrous iron added ($Fe(II)_T$) and the free $Fe^{+2}$ measured polarographically can be attributed to complexation of the iron by tannic acid. (The elimination of oxygen from the polarographic cell precludes the disapperance of Fe(II) by oxidation.) If one assumes, for purposes of simplicity, the formation of a 1:1 ferrous-tannate complex, then

$$Fe^{+2} + TA^- = Fe\text{—}TA^+ \qquad (2)$$

The stability constant, *K*, for this ferrous-tannate complex is

$$K = \frac{[Fe\text{—}TA^+]}{[Fe^{+2}][TA^-]} \qquad (3)$$

and its magnitude can be calculated from the data of Table II, employing mass balances for ferrous iron and tannic acid:

$$[Fe(II)]_T = [Fe^{+2}] + [Fe\text{—}TA^+] \qquad (4)$$

and

$$[TA]_T = [HTA] + [TA^-] + [Fe\text{—}TA^+] \qquad (5)$$

where HTA is the concentration of undissociated tannic acid. Tannic acid has an acidity constant of about $10^{-5}$ (Hem, 1960)

$$K_a = \frac{[H^+][TA^-]}{[HTA]} \qquad (6)$$

By use of Equations 3 through 6 and the experimental values for $Fe(II)_T$, $Fe^{+2}$, and $[TA]_T$ from Table II, an average value for $K$ of $9.5 \times 10^3$ can be calculated. This value is in reasonable agreement with Hem's revised estimate of the ferrous-tannate complex of $10^6$ (1973) and that reported by Schnitzer and Skinner (1966) of $K = 10^{5.8}$ for complexes of ferrous iron and polyphenolic soil leachates. All of these values can be considered as representative of complexes between ferrous iron and humic material, but cannot be used as absolute values because of the complex nature of the natural humics. The fact that the calculated $K$ is in general agreement with previously published values suggests that the 1:1 ferrous-tannate complex is a good approximation. It should also be emphasized that while the data of Table II are in basic qualitative and semiquantitative agreement with previous polarographic investiation by Oldham and Gloyna (1969), the results of the present study are of a single compound (tannic acid) for which the molecular structure is known (Hem, 1960) and not for a combination of leachates of an unspecified structure. Thus, the stability constant reported here is a somewhat more meaningful chemical quantity.

Results of polarographic studies employing ferric iron and tannic acid are summarized in Table III. Due to extensive hydrolysis and precipitation of Fe(III) above pH 3 (thereby preventing reduction at the Hg surface), the investigation was confined to the acidic pH range. As in the case of ferrous iron, Table III indicates that for ferric iron the diffusion current ($Fe^{+3}$) decreases as the organic-iron ratio increases. The disappearance of $Fe^{+3}$ can be attributed to reduction by tannic acid or to complexation with tannic acid, the extent of such reactions increasing as the pH increases from 1.5 to 3.0. (The free $[Fe^{+3}]$ as measured by the diffusion current in Table III decreases with increasing pH.) Previous studies by the authors (Theis and Singer, 1973) indicated that, in this pH range, much of the Fe(III) is reduced. The fact that a rather small concentration of tannic acid ($10^{-5}M$) results in the disappearance of as much as $6 \times 10^{-5}M$ $Fe^{+3}$ at pH 1.5 is further evidence for chemical reduction of Fe(III) by tannic acid. Still, the possibility of complexation of Fe(III) cannot be ruled out in view of the number of references to it in the literature.

**Table III. Polarographic Results for Ferric Iron and Tannic Acid in 1*M* KCl**

| pH | Fe(III), *M*/1 | Tannic acid, *M*/1 | Diffusion current, µamp | $Fe^{+3}$, *M*/1 |
|---|---|---|---|---|
| 1.5 | $4.3 \times 10^{-4}$ | 0.0 | 2.60 | $4.3 \times 10^{-4}$ |
| | | $1 \times 10^{-5}$ | 2.00 | $3.7 \times 10^{-4}$ |
| | | $5 \times 10^{-5}$ | 1.80 | $3.3 \times 10^{-4}$ |
| | | $1 \times 10^{-4}$ | 1.35 | $2.5 \times 10^{-4}$ |
| | | $5 \times 10^{-4}$ | 0.80 | $1.5 \times 10^{-4}$ |
| | | $1 \times 10^{-3}$ | 0.35 | $\sim 1 \times 10^{-5}$ |
| 2.0 | $4.3 \times 10^{-4}$ | 0.0 | 2.10 | $4.3 \times 10^{-4}$ |
| | | $1 \times 10^{-5}$ | 1.80 | $3.8 \times 10^{-4}$ |
| | | $5 \times 10^{-5}$ | 0.75 | $1.6 \times 10^{-4}$ |
| | | $1 \times 10^{-4}$ | 0.40 | $\sim 1 \times 10^{-5}$ |
| | | $5 \times 10^{-4}$ | 0.35 | $\sim 1 \times 10^{-5}$ |
| | | $1 \times 10^{-3}$ | 0.0 | 0 |
| 3.0 | $4.3 \times 10^{-4}$ | 0.0 | 1.80 | $4.3 \times 10^{-4}$ |
| | | $1 \times 10^{-5}$ | 1.28 | $3.3 \times 10^{-4}$ |
| | | $5 \times 10^{-5}$ | 0.75 | $1.8 \times 10^{-4}$ |
| | | $1 \times 10^{-4}$ | 0.35 | $\sim 1 \times 10^{-5}$ |
| | | $2 \times 10^{-4}$ | 0.17 | $<10^{-5}$ |

The effects of organic matter on the rate of oxidation of ferrous iron (shown in Figures 1 and 2) can be interpreted in terms of metal-organic complexation superimposed on Fe(II) oxidation if one considers the following interrelated reactions:

$$Fe^{+2} + O_2 \xrightarrow{k_1} Fe^{+3} \tag{7a}$$

$$Fe^{+2} + \text{org.} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Fe(II){-}\text{org} \xrightarrow[k_4]{+O_2} Fe(III) \tag{7b}$$

$$K = k_2/k_3 \tag{7c}$$

where the $k$'s represent rate constants and $K$ is the stability constant of the ferrous-organic complex. There are four cases of interest as follows:

(a) $K$ small, $k_4 << k_1$
(b) $K$ large, $k_4 << k_1$
(c) $K$ moderate, $k_1 >> k_3$, $k_4 << k_1$
(d) $K$ large, $k_4 >> k_1$

For Case a, little ferrous iron is tied up in a complex and the oxidation proceeds very nearly in accordance with the rate in simple aqueous media (Stumm and Lee, 1961) via reaction 7a. This is illustrated schematically by curve (a) in Figure 5, and explains the results for vanillic acid, vanillin, phenol, resorcinol, syringic acid, and histidine described by Figure 1.

Case b describes the formation of a sizable oxidation-resistant complex. Most of the $Fe^{+2}$ is complexed and resists oxidation. The relative magnitude of $k_4$ compared to $k_1$ will determine whether there is complete inhibition, as illustrated by curve (b), or partial inhibition shown by (b′) in Figure 5. Tannic acid and glutamine, respectively, illustrate these two effects. Tannic acid ties up a sizable fraction of the Fe(II), leaving little free $Fe^{+2}$ to react with oxygen according to simple kinetics, and oxidation takes place through the Fe(II)-organic complex (Reaction 7b).

Case c involves the oxidation of free ferrous iron in equilibrium with the complex. The iron, which is irreversibly complexed, is neither released nor oxidized. Such an effect is shown by curve (c) of Figure 5. There is an initial oxidation of the free $Fe^{+2}$ but a gradual leveling off as $Fe^{+2}$ is depleted, such as occurred with tannic acid in Figure 2. Case c can be considered a special form of Case b.

Finally, Case d is a possible explanation for the acceleration of the oxidation rate as found with citric acid. It involves the formation of a strong complex with $Fe^{+2}$ that enhances the oxidation reaction, $k_4$ being greater than $k_1$. Curve (d) of Figure 5 illustrates this case.

Unfortunately, the complexity of the reactions do not allow a more rigorous quantitative treatment of the data. For such a treatment, the precise steps involved in each reaction must be known. This is simply not the case, particularly in the slow oxidation reaction of the ferrous-organic complex which was indicated by manometric studies. Nevertheless, the agreement of the curves of Figure 5 with those actually found for the organic compounds studied is indicative of the probable manner in which ferrous iron and organic matter interact.

The results of this investigation coupled with the results of other studies have led to the development of a model to explain the behavior of iron in the presence of humic substances. A schematic of this model is given in Figure 6. In the absence of appreciable quantities of dissolved organic matter, ferrous iron is oxidized quite rapidly upon the introduction of oxygen to ferric iron which precipitates as $Fe(OH)_3$ and is removed from the system (Reactions 1

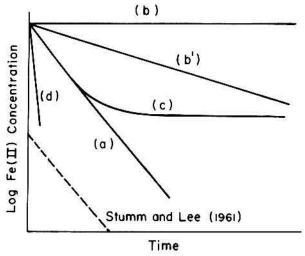

**Figure 5.** Schematic curves depicting kinetics of oxidation of ferrous iron in presence of Fe(II)-complexation by organic matter as described by Reactions 7a through 7c

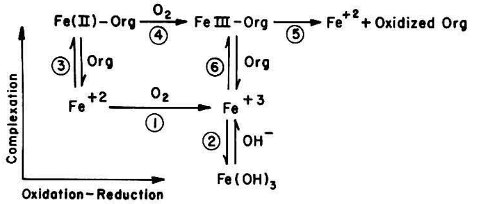

**Figure 6.** Schematic diagram of model which describes behavior of iron in presence of organic matter and oxygen. Complexation reactions are indicated vertically, while redox reactions are indicated horizontally

and 2 of Figure 6). If significant concentrations of organic matter are present, the complexation reaction with ferrous iron (Reaction 3) will compete with the oxygenation reaction. The fractions of ferrous iron complexed or oxidized will depend on the pH and the quantity and type of organic matter present. Oxidation of the complexed ferrous iron (Reaction 4) proceeds via a slow step (manometric studies plus visual observations indicate it may be several days before significant amounts of ferrous iron are oxidized) to form the corresponding ferric complex with the organic matter. The resultant Fe(III) is unstable and is reduced by the organic compound (Reaction 5). The ferrous iron is free to participate in the cycle again. The oxidized organic matter may still be capable of complexing iron again, and may participate in the cycle until it is oxidized to an inert form. The rate of Reaction 5 is dependent on the specific type of organic compound that is complexed with the iron.

An additional competition exists for the ferric iron between the organic species and hydroxide (Reactions 2 and 6). Again, pH is a determining factor in regard to the relative proportions of ferric iron complexed by organic matter (Reaction 6), reduced by the organic compounds (Reaction 5), or complexed by hydroxide (Reaction 2).

The model of Figure 6 differs from the behavior indicated by Reaction 1a through 1c by the addition of Reactions 3 and 4—namely the complexation of Fe(II) and subsequent slow oxidation to the corresponding Fe(III) complex. These two reactions provide an explanation for the slow rate of oxygen consumption by the iron-organic system.

Aqueous iron behaves according to the model of Figure 6 because of the relative ease with which the ferrous-ferric couple can undergo reversible oxidation and reduction. However other metals, notably manganese and cobalt, also possess this property such that the potential pathways are not specific for iron. In addition, the complexing ability of the organic matter for other metals (regardless of their redox characteristics) plus the adsorptive capacity of hydrous ferric oxide for other metals indicates that the model presented may have a significant effect on the availability and distribution of other trace elements in natural waters.

## *Conclusions*

Iron, in both the ferrous and ferric forms, can be stabilized in an aqueous environment by dissolved organic matter in amounts in excess of that predicted by simple thermodynamic and kinetic considerations. Ferrous iron is capable of forming complexes with organic matter and, as such, is resistant to oxidation even in the presence of dissolved oxygen. The relative strength of such complexes is illustrated by the ferrous-tannate complex that has a stability constant of approximately $10^4$.

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# Synergistic Inhibition of Apparent Photosynthesis Rate of Alfalfa by Combinations of Sulfur Dioxide and Nitrogen Dioxide

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■ Alfalfa was exposed in environmental chambers to combinations of sulfur dioxide ($SO_2$) and nitrogen dioxide ($NO_2$) at concentrations ranging from 15–50 pphm of each gas in 1- and 2-hr fumigations. Inhibition of apparent photosynthetic rate [carbon dioxide ($CO_2$) uptake rate] due to the presence of each gas alone and to combinations of both gases was measured. While 2-hr exposure to 25 pphm $SO_2$ produced 2–3% inhibition and exposure to 25 pphm $NO_2$ produced no measurable depression, exposure to both gases at 25 pphm produced 9–15% inhibition. Concentrations of $SO_2$ and $NO_2$ required to measurably depress the apparent photosynthetic rate were reduced when both gases were applied; a mixture of 15 pphm of each gas caused a 7% decrease. The degree of synergism decreased as concentrations increased—50 pphm of both gases did not elicit synergistic response.

Situations in which only one air pollutant is present in an airshed are rare. Urban sources emit one or more pollutants into air already contaminated by a large number of substances. Many sources emit two or more major pollutants. Coal-fired power plants, for example, produce both sulfur dioxide and nitrogen oxides as well as particulate matter. The need for research into the adverse effects of combinations of air pollutants is therefore apparent.

The phytotoxicity of the major air pollutants has been studied, and concentrations required to produce injury and reduce photosynthetic rate have been reported for many plant species. Less is known, however, about the effects of combinations of pollutants on vegetation. The possibility of nonadditive (synergistic or antagonistic) response of plants to combinations of phytotoxic air pollutants has only recently been given consideration.

A number of authors have reported decreased injury threshold concentrations and potentiation of injury symptoms due to combinations of ozone ($O_3$) and sulfur dioxide. Injury to Eastern white pine (Jaeger and Banfield, 1970; Dochinger et al., 1970), peanuts (Applegate and Durrant, 1969), and tobacco (Grosso et al., 1971; Menser and Heggestad, 1966) has been attributed to exposure to $SO_2$–$O_3$ mixtures.

Data for other combinations of pollutants are more limited. Tingey et al. (1971) have reported that while the $NO_2$ injury threshold for several crop species in a 4-hr fumigation is about 200 pphm and the $SO_2$ threshold is about 50 pphm over 4 hr, injury developed when these plants were exposed to mixtures of less than 25 pphm of each gas for 4 hr.

Another area of research concern has been determining whether growth suppression may result from concentrations of air pollutants that do not result in visible injury. Hull and Went (1952) reported that alfalfa, endive, sugar beet, and tomato plants grown in the ambient air at Pasadena, Calif., were smaller than those grown in charcoal filtered air. A study with Bel-B tobacco (Menser et al., 1964) indicated that the ambient air at Beltsville, Md., also can reduce plant growth even in the absence of visible injury. Hill and Bennett (1970) have shown that $NO_2$ and NO inhibit apparent photosynthesis of oats and alfalfa at concentrations below those required to cause visible injury. The threshold concentration for photosynthetic effects due to oxides of nitrogen appeared to be about 60 pphm in 2-hr fumigations. Sulfur dioxide, too, has been shown to decrease apparent photosynthetic rate, with effects beginning at approximately 20 pphm $SO_2$ (Bennett and Hill, 1973; Thomas and Hill, 1937).

The purpose of this study was to determine whether combinations of $SO_2$ and $NO_2$ would elicit a synergistic effect in decreasing photosynthetic rate in alfalfa.

## *Methods and Materials*

Alfalfa (*Medicago sativa* L. var. Ranger) was grown under greenhouse culture in 1-gal pots and redwood flats measuring 36 × 53 × 20 cm. Plants varied from 30–45 cm in height at fumigation.

Plant fumigations were conducted in the airtight, internal recirculation environmental chambers previously described by Hill (1967). Thirty-six pots or six flats were placed in each of two identical chambers, and fumigation was begun when carbon dioxide uptake rate had stabilized. One chamber served as a control; the $CO_2$ uptake rate in the fumigation chamber is reported as percent of control chamber uptake. Temperature was maintained at 25 ± 2°C and relative humidity between 50 and 60%. Illumination was provided by air- and water-cooled light banks consisting of 33 fluorescent lights, one uv emitting fluorescent light, six 150-W tungsten lamps, and six 500-W quartz iodide lights. The light intensity at plant height was 45–50 klux. Temperature and relative humidity were controlled by recirculating the air through cooling and condensing coils before re-entering the plant compartments. Wind velocity above the plants was 1.2–1.5 m $sec^{-1}$.

Apparent photosynthesis rate was determined by adding pure carbon dioxide serially into each chamber through a solenoid-controlled valve. Carbon dioxide addition flow rate was measured with glass flow meters, and its concentration within the chambers was monitored with a Beckman IR215 $CO_2$ infrared analyzer connected to a recorder equipped with a microswitch control point. The control point was set at the equivalent of 330 ppm $CO_2$ concentration. When this $CO_2$ level was reached in each environmental chamber, a solenoid valve controlling $CO_2$ flow was closed. A time delay system regulated the interval the solenoid remained closed before subsequent $CO_2$ flows were permitted into the chambers. The times of occurrence for each impulse were recorded by a Simplex Time Event Recorder and from these data, in conjunction with the $CO_2$ flow rates, $CO_2$ uptake rates were computed.

Pollutant concentrations within the fumigation chamber were regulated by a system similar to that described for controlling $CO_2$ concentrations. Nitrogen dioxide, NO, and $SO_2$ were diluted and pressurized with nitrogen in separate tanks before being added to the fumigation chamber through solenoid control valves. The pollutant

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concentrations were monitored continuously by analyzers whose outputs were fed to recorders equipped with microswitch sensors controlling pollutant flow solenoid valves. Sulfur dioxide was measured with a Melloy 1100-B Flame Photometric Sulfur Analyzer and a Beckman 906 $SO_2$ analyzer. The modified West-Gaeke spectrophotometric method of Scaringelli et al. (1967) was used to substantiate $SO_2$ levels during fumigations.

Nitrogen dioxide and NO concentrations were measured with a Mast Ozone Meter; NO was converted to $NO_2$ by use of "dichromate" papers (Wilson and Kopczynski, 1968). In fumigations in which both $SO_2$ and $NO_2$ were present in the chamber these same dichromate papers were used to remove $SO_2$, which causes negative interference in the Mast response, from the sample stream (Saltzman and Wartburg, 1965). Total oxides of nitrogen ($NO_x$) were therefore measured in the combination studies. In $NO_2$ fumigations, it was observed that NO was produced in the chamber by reduction of $NO_2$ and, since NO is removed at approximately $1/20$ the rate at which $NO_2$ is removed by the plants (Hill, 1971), its concentration in the chamber increased from zero to no more than a third of the $NO_x$ concentration. Most sources of nitrogen oxides emit both NO and $NO_2$ and the two gases exist in chemical equilibrium in the atmosphere. Since NO is thus nearly always present in the atmosphere when $NO_2$ is present and NO–$SO_2$ combinations did not appear to elicit synergistic response, this buildup was not considered a serious problem. The colorimetric methods of Saltzman (1965) and Nash (1970) were used to corroborate chamber $NO_2$ and $NO_x$ concentrations.

All analyzers and wet chemical methods were calibrated against known concentrations of $SO_2$ and $NO_2$ produced by $SO_2$ and $NO_2$ permeation tubes (Scaringelli et al., 1970) and by a dynamic flow method similar to that reported by Thomas and Amtower (1968).

Four types of fumigations were run: (1) $NO_x$ or $SO_2$ alone for 1- and 2-hr periods, (2) $NO_x$ and $SO_2$ simultaneously for 1 and 2 hr, (3) $NO_x$ alone for 1 hr, then both $NO_x$ and $SO_2$ during the second hour, and (4) $SO_2$ alone for 1 hr, then $SO_2$ and $NO_x$ during the second hour.

### *Results and Discussion*

Combinations of $SO_2$ and $NO_2$ inhibited apparent photosynthesis in alfalfa to a greater degree than would be expected from summing the effects due to each pollutant alone at the same concentrations. Also, concentrations well below those required to cause measurable photosynthesis depression in fumigations with $SO_2$ or $NO_2$ alone were found to inhibit $CO_2$ uptake rate when both gases were applied. Table I lists data obtained in each type of fumigation. The synergistic effect was most marked at the lower concentrations used and decreased as concentrations increased. At 50 pphm of each gas no synergism was observed.

The data for $SO_2$ indicate that the concentration below which photosynthetic inhibition cannot be measured with our system (approximately 2% change in $CO_2$ uptake rate) is between 20 and 25 pphm. This agrees with data reported by Thomas and Hill (1937) in which fumigation with 24 pphm $SO_2$ was found to have no effect on photosynthetic rate over a 3-day period. The average $CO_2$ uptake rate of alfalfa exposed to 25 pphm $SO_2$ for 1 hr was 98 ± 2% of the uptake rate measured for the control.

The $NO_2$ threshold concentration required to measurably depress photosynthetic rate in 2-hr fumigations of alfalfa is approximately 60 pphm as previously determined at this laboratory (Hill and Bennett, 1970). Two-hour fumigations with 25 pphm $NO_2$ did not produce significant $CO_2$ uptake rate inhibition.

**Table I. Inhibition of $CO_2$ Uptake Rates of Alfalfa (Percent of Control) Due to Exposure to $SO_2$, $NO_x$ and NO, and Combinations of These Gases in 1- and 2-Hr Fumigations**

| Fumigation type | Pollutant concn, pphm | | | No. of replications | Av. depression of $CO_2$ uptake rate, % | Std dev |
|---|---|---|---|---|---|---|
| | $SO_2$ | $NO_x$ | NO | | | |
| $SO_2$ only | 25 | | | 15 | 2 | 2 |
| | 35 | | | 5 | 8 | 4 |
| | 42 | | | 3 | 11 | 3 |
| | 50 | | | 7 | 22 | 3 |
| $NO_x$ only | | 25 | 10 | 13 | 0 | 2 |
| | | 40 | 15 | 4 | 2 | 2 |
| $SO_2$ + $NO_x$ simultaneous application | 15 | 15 | 5 | 4 | 7 | 2 |
| | 25 | 25 | 10 | 13 | 9[a] | 3 |
| | 35 | 30 | 10 | 3 | 16 | 2 |
| | 50 | 40 | 15 | 7 | 20 | 4 |
| Sequential, $SO_2$ 1st hr | 25 | 25 | 10 | 16 | 13[a] | 4 |
| Sequential, $NO_x$ 1st hr | 25 | 25 | 10 | 14 | 15[a] | 4 |

[a] Values significantly different at 99% confidence interval from sum of response due to $SO_2$ and $NO_x$ alone at corresponding concentrations.

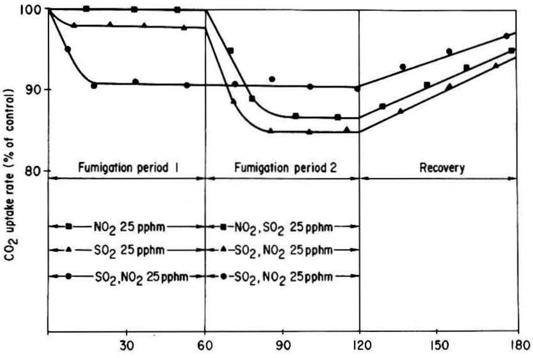

**Figure 1.** Photosynthesis inhibition and recovery rates induced by combinations of $SO_2$ and $NO_2$ at 25 pphm in three types of studies

Studies in which alfalfa was exposed to a mixture of 25 pphm of $SO_2$ and $NO_2$ in 1- and 2-hr fumigations, which would be expected to inhibit apparent photosynthetic rate by no more than 2–4% if the effects were additive, produced from 9–15% inhibition. Two statistical methods, the two sample t-test and the Mann-Whitney-Wilcoxon test (Steel and Torrie, 1960), were used to show nonadditivity at the 99% confidence interval. A mixture of 15 pphm of each gas reduced photosynthetic rate by 7% in 2-hr fumigations. The sequential studies, in which plants were exposed during the first hour to one pollutant after which the other pollutant was added to the first during the second hour, did not produce a significantly greater effect than did simultaneous application of both pollutants.

Initial studies were run to determine whether $NO_2$ or NO was more responsible for the synergistic response observed in combination with $SO_2$. Since $NO_2$ may be reduced to NO and some NO is oxidized to $NO_2$ as it enters the chamber at high concentration, an evaluation of each gas separately in combination with $SO_2$ was not possible. However, increasing the ratio of NO to $NO_x$ for a given $NO_x$ concentration decreased the degree of synergism, indicating that NO had little or no effect.

Figure 1 shows composite graphs of $CO_2$ uptake rate vs. time for fumigations with 25 pphm $SO_2$ and $NO_2$. In all fumigations the $CO_2$ uptake rate inhibition was complete within about 20 min, after which the rate remained quite stable over a 2-hr period. The sequential studies in which $SO_2$ is added first demonstrate the synergism strikingly. The inhibition due to $SO_2$ alone at 25 pphm was measured during the first hour; a decrease in $CO_2$ uptake rate due to addition of the $NO_2$ at 25 pphm (which causes no effect when added alone) during the next hour shows that the response is nonadditive.

So long as tissue injury does not occur, photosynthetic rate inhibition due to fumigation with $SO_2$ and/or $NO_2$ is reversible. Depending upon the degree of inhibition, recovery of $CO_2$ uptake rate to control levels was complete within 30 min to 2 hr.

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# Poly-β-hydroxyalkanoate from Activated Sludge

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■ A new heteropolymer has been isolated by chloroform extraction of activated sludges supplied by the Greater Peoria Sanitary District and from the waste purification facility of an industrial grain-processing plant. The compound is a polyester with physical and chemical properties similar, but not identical, to those of poly-β-hydroxybutyrate (PHB). The polyhydroxyalkanoate (PHA) is composed primarily of β-hydroxyvaleric and β-hydroxybutyric acids, along with lesser amounts of higher molecular weight components. It melts at 97–100°C, whereas PHB melts at 160–170°C. Because PHA is soluble in hot 95% ethanol, it can be separated from the alcohol-insoluble PHB. Gas chromatographic analysis of products obtained by hydrogenolysis and by saponification of PHA has given evidence for a mixture of $C_4$, $C_5$ (major component), $C_6$, and $C_7$ components. Structural studies show PHA to be a new microbial polymer present in activated sludge.

Activated sludge is a gray-black, flocculent, sticky material formed during the microbial oxidation of raw sewage. Wallen and Davis (1972) have shown that activated sludge contains microbial cells, heteropolysaccharides, and a polyester. Crabtree et al. (1966) implicated polyhydroxybutyrate (PHB) as a factor responsible for the flocculation properties of activated sludge, but Deinema (1972) has refuted this claim. However, PHB often serves as an endogenous reserve nutrient for some bacterial cells when their extracellular carbon sources are depleted (Macrae and Wilkinson, 1958). The concentration of PHB in samples of activated sludge from domestic sewage was reported by Deinema (1972) to range from 0.0–0.2% on a dry weight basis. Now we are reporting further work on the identification of the polyester present as 1.3% of the dry weight of activated sludge obtained from the Greater Peoria Sanitary District. The polyester also is present in sludge from the commercial treatment facility of a grain-processing plant in Pekin, Ill. It is a new compound being reported as a component of activated sludge.

## *Materials and Procedures*

Gas chromatography (gc) of derivatives was done in ¼-in. 4-ft columns of either 10% SP-1000 modified Carbowax, 20% SE-30, or 3% SE-52 silicone columns. Isothermal determinations with SP-1000 columns were run at 100° and 120°C, whereas programmed analyses were begun isothermally for 1 min at 100°C and then heated to 230°C at a rate of 20°C/min. All runs made on SE-52 and SE-30 columns were isothermal at 125°C for 1 min and then programmed at 15°C/min to a maximum of 275°C. Trimethylsilyl (TMS) esters and ethers were prepared with Tri-Sil/BSA reagent (Pierce Chemical Co., Rockford, Ill.).

Nuclear magnetic resonance (nmr) spectra were obtained on a Varian HA-100 spectrometer from deuterochloroform solutions of a known sample of PHB and of the isolated polyester [polyhydroxyalkanoate (PHA)].

Gc and mass spectroscopy (gc/ms) were combined for analysis of the methyl esters of saponification reaction products. A Nuclide Model 12-90G mass spectrometer, in conjunction with a computer, provided printed mass spectra of the individual components separated by gc.

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Infrared (ir) spectra were obtained on a Beckman Model IR-8 spectrometer by internal reflection spectroscopy in the solid state from material deposited by evaporation of chloroform solutions onto a 2-mm KRS-5 plate (Wilks Scientific Corp., South Norwalk, Conn.). Gc effluent was entrapped in a Wilks chilled collector containing two KRS-5 plates, each 1.27 mm thick. Ultraviolet (uv) spectra were recorded on a Beckman Acta III scanning spectrometer from sulfuric acid solutions of PHA and PHB.

All melting points were determined with a Fisher-Johns apparatus and are uncorrected. Samples of authentic PHB from *Bacillus megaterium* NRRL B-1827 were supplied by W. C. Haynes (NRRL). Activated sludge was obtained from waste treatment facilities of the Greater Peoria Sanitary District and CPC International of Pekin, Ill.

## *Results*

**Isolation.** A slurry of activated sludge was centrifuged and the semidry sludge extracted several times with hot water. Subsequent drying and extraction of the sludge with either benzene or chloroform gave a black solution. Evaporation of solvent gave a black gummy mass. When this material was washed with either hexane or ether to remove unwanted products, an insoluble residue remained, originally thought to be PHB because of its known insolubility in these solvents. Furthermore, the solubility characteristics of the residual material were similar to PHB, and the implication of PHB in the sewage flocculation process (Crabtree et al., 1966) made such a conclusion logical. In addition, the unknown material, like PHB, formed films when chloroform solutions were evaporated.

Chloroform extracts of activated sludge contain both PHB and PHA. The latter is soluble in hot ethanol (95%) making possible its separation from PHB (identified by ir) as well as from other occluded impurities derived from the sludge. PHA is also soluble in acetone (with warming), hot methanol, benzene, chloroform, tetrahydrofuran, and pyridine.

**Analysis.** The procedure of Slepecky and Law (1960) for the detection of PHB in biological materials was followed in analyzing PHA. A sample of PHA was heated 1 min in concentrated sulfuric acid, cooled, and scanned by uv. Under these conditions, PHB gave an absorption maximum at 235 nm, indicative of crotonic acid. Because our product absorbed uv at the same value, we could draw no conclusions. Thus both PHA and PHB give a value showing the presence of crotonic acid derived from the dehydration of $\beta$-hydroxybutyric acid moieties in each compound. Care should therefore be exercised when using this assay procedure because it is not specific for PHB. It is likely that PHA has been found in sludge or in bacterial cultures but was reported erroneously as PHB.

Further comparison with PHB showed that our product differed in several ways. It melted at 100–105°C, but repeated washing with hexane reduced this value to 97–100°C; PHB melts at 160–170°C. When subjected to ir analysis, major differences were noted between its spectrum and that of PHB. For example, the ir absorption for methyl and methylene groups differs in the 2870–2990 cm$^{-1}$ region; also, PHB has more detailed sharp bands in the "fingerprint" range between 1000–1400 cm$^{-1}$ (Figure 1). Our product and PHB show strong ester carbonyl bands at 1723 and 1725 cm$^{-1}$, respectively.

The nmr spectrum (Figure 2) of the isolated sludge-derived product indicated that it contained $\beta$-hydroxybutyric acid and possibly $\beta$-hydroxyvaleric acid. Bands at 9.0, 9.1, and 9.2 $\tau$ show the presence of a $CH_2$ group joined to a $CH_3$. These bands were absent in the spectrum for authentic PHB. Other bands in the polyester spectrum appeared at 8.2–8.5 $\tau$ (also missing for PHB). These indicated the presence of a $CH_2$ group, a moiety not found in PHB.

When heated in a test tube, PHA gave a strong odor of crotonic acid (confirmed by gc) and a solid residue formed which retained some ir absorption characteristics of unheated PHA. When analyzed for carbon and hydrogen content, the compound contained 60.62% C and 8.06% H. These values approximate those for a compound containing a hydroxyvalerate moiety. Because the presence of hydroxybutyrate would lower the values for C and H, it is likely that the material also contains a structural unit having more than 5 carbon atoms.

**Structure Studies.** A gc separation of oils obtained by thermal degradation of PHA (235°C) was done on a 10% SP-1000 column and on a 3% SE-52 column. Two components showed retention times identical to those of crotonic acid and 2-pentenoic acid, respectively. The known tendency of $\beta$-hydroxy acids to dehydrate to unsaturated acids indicates that the crotonic and 2-pentenoic acids in the oil from destructive distillation of PHA were formed by dehydration of $\beta$-hydroxybutyric and $\beta$-hydroxyvaleric acids, respectively.

Saponification of PHA by refluxing 1 hr with dilute (2.0%) NaOH in 50% methanol gave a mixture of the sodium salts of organic acids. Acidification, followed by extraction with ether, gave a mixture having an odor characteristic of low-molecular-weight aliphatic acids. These were derivatized with Tri-Sil/BSA to form TMS esters and ethers suited for gc on a 3% SE-52 column. Forming a

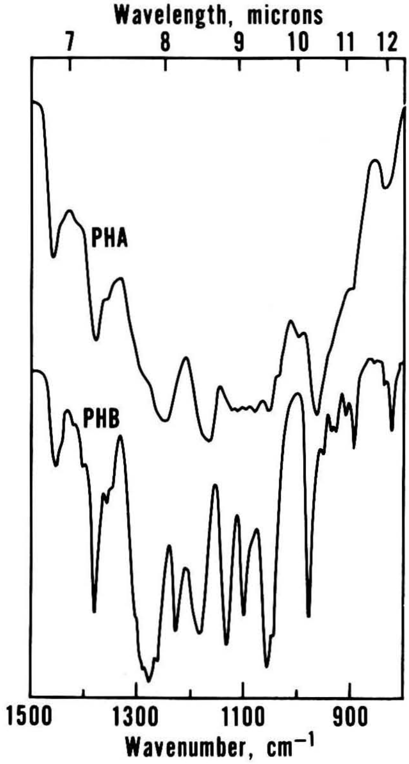

**Figure 1.** Infrared spectra of polyhydroxyalkanoate (PHA) and poly-$\beta$-hydroxybutyrate (PHB)

TMS ether with the β-hydroxyl group, in addition to the usual TMS esters of carboxyl groups, was expected to preclude dehydration and give peaks representative of any β-hydroxy acids or aliphatic nonhydroxylated acids present. The TMS derivatives were analyzed by ms combined with gc. Crotonic acid and β-hydroxybutyric acid were identified by this procedure, using TMS derivatives of authentic samples of acids. Although some cleavage of the TMS group occurred which made interpretation difficult, the ms data was normalized to show that 2-pentenoic acid was also present, indicative of its precursor, β-hydroxyvaleric acid. The largest peak had a retention time consistent for β-hydroxyvaleric acid. A fifth gc peak had a retention time intermediate to that for a $C_5$ monounsaturated acid and β-hydroxybutyric acid. As no interpretation could be made from a mass spectrum, an eluted gc sample of the unknown product was trapped between two chilled KRS-5 plates for ir analysis by internal reflection spectroscopy. Unexpectedly, the spectrum showed no unsaturation present; the compound may be an alkanoic or hydroxyalkanoic acid.

Hydrogenolysis of 0.5 gram of PHA with aluminum hydride (Alane, 0.87*M*) in benzene (Lithium Corp. of America, Bessemer City, N.C.) for 48 hr gave 0.11 gram of oily material. Silylation and analysis by gc/ms confirmed the presence of a $C_4$ and $C_5$ diol. The diols are the compounds expected to be formed by cleavage of ester linkages and subsequent reduction. Identified as 1,3-butanediol and 1,3-pentanediol, respectively, they confirmed the presence of β-hydroxybutyric and β-hydroxyvaleric acids in PHA as a polyester.

When temperatures were lowered (100°C) in conjunction with an SP-1000 column, a gc/ms analysis of methyl esters of saponified PHA gave identification data for a $C_4$, $C_5$, $C_6$, and possibly a $C_7$ hydroxy acid as components of the reaction mixture. The $C_5$ β-hydroxy acid predominates, with $C_4$ next in abundance, whereas the higher homologs are present in minor amount only. The ratio of $C_5$ to $C_4$ β-hydroxy acids is 5 to 1, based upon integration (Disc integrator) of gc peaks. The $C_6$ peak was identified by ms as methyl β-hydroxyhexanoate (Figure 3). A very small gc peak with a higher retention time was presumed to be the methyl ester of a $C_7$ hydroxy acid. However, the mass spectrum lacked sufficient data to confirm the identity of the compound unequivocally; thus it is not certain that it is a $C_7$ component of PHA. A comparison of the properties of PHA and PHB are summarized in Table I.

*Discussion*

We have not been able to produce PHA in vitro from microbial species isolated from activated sludge provided by the Peoria District or from CPC International sludge, even though PHA was isolated from both samples. Possibly PHA production depends upon formation of essential precursors by more than one microorganism in a mixed bacterial population.

The β-hydroxy acids which comprise PHA can be produced as intermediates in the metabolic degradation of higher molecular weight fatty acids via β-oxidation; thus their presence is to be expected in sewage. However, the predominance of a $C_5$ hydroxy acid is of interest because it would be derived from odd-numbered fatty acids which are less common than those having even-numbered carbon chains. The presence of microbial β-hydroxyvaleric (3-

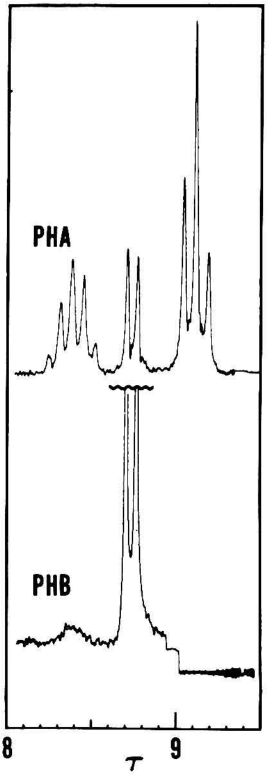

Figure 2. Nuclear magnetic resonance spectra of PHA and PHB

**Table I. Physical Properties of PHA[a] and PHB**

| PHA | PHB |
|---|---|
| White solid | White solid |
| Soluble in $CHCl_3$; precipitated with ether | Soluble in $CHCl_3$; precipitated with ether |
| Melting point, 97–100°C | Melting point, 160–170°C |
| Soluble in hot ethanol | Insoluble in hot ethanol |
| Forms film by evaporation of $CHCl_3$ solution | Forms film by evaporation of $CHCl_3$ solution |
| Heteropolymer containing $C_4$, $C_5$, and $C_6$ hydroxy acids | Homopolymer containing a $C_4$ hydroxy acid |

[a] PHA = polyhydroxyalkanoate; PHB = poly-β-hydroxybutyrate.

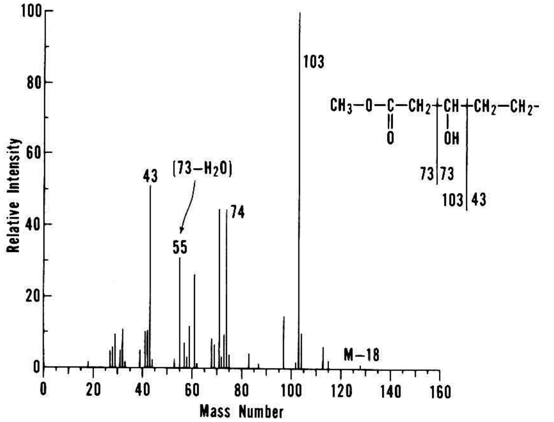

Figure 3. Mass spectrum of methyl β-hydroxyhexanoate

hydroxypentanoic) acid as a major component of PHA is unique inasmuch as the compound is not recognized as a common product of microbiological activity (Asselineau, 1966). We feel that PHA is a microbial product because it is related to the polyester, PHB, which is produced by many bacteria; both compounds have structural and physical properties that are similar. Furthermore, the presence of PHA in grain-derived activated sludge samples from CPC International as well as from the domestic sewage-derived activated sludge of the Greater Peoria Sanitary District facility indicates that the polyester is not present in the raw sewage entering these plants. The raw sewage coming from the CPC International plant contains washings from normal grain processing plant operations, and would not be expected to contain insoluble PHA. It is formed instead within a 2-hr period of aerobic growth under conditions of intensive oxidation. We have subjected samples of activated sludge containing PHA to further oxidation over a 20-hr period. The weight of PHA recovered was 44% of the original weight prior to oxidation. The polyester is thus biodegradable under conditions of prolonged oxidation.

The polyesters reported by Kolattukudy and Purdy (1973) in sludge are of longer ($C_{16}$–$C_{18}$) chain length and were isolated from digested, or anaerobic, sludge, the end product of 20 days of anaerobic growth. Our compound was found in activated sludge, formed during a 2-hr aerobic process. The variety of homologous hydroxy acids present in PHA demonstrates the unique ability of microorganisms to synthesize unusual compounds ordinarily difficult or impossible to attain by synthetic routes. In activated sludge, the presence of PHA is an example of the potential variety of materials to be obtained from waste treatment facilities.

Polyesters have been chemically synthesized from $\alpha$-hydroxy esters. A patent issued to Filachione et al. (1950) describes a process for forming polyesters from methyl lactate and higher homologs, using sulfuric or $p$-toluenesulfonic acid as a catalyst. The products were prepared from the acetate, propionate, butyrate, and several other $\alpha$-hydroxylated esters. Such $\alpha$-hydroxy esters are quite different in stability and mode of reactivity from $\beta$-hydroxy esters and acids.

### *Acknowledgment*

We thank C. A. Glass for nmr results, E. A. Selke for a mass spectral identification of 2-pentenoic acid, and C. A. McGrew for elemental analyses.

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# Photostationary State in Photochemical Smog Studies

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■ The photostationary equilibrium predicted by Leighton and others holds over most or all of several smog chamber experiments. However, late in the reaction of a "reactive" hydrocarbon, the equilibrium becomes unbalanced due to competition of reactive (radical) species for nitric oxide. Accurate measurement of low concentrations of NO at the late stages of these reactions allows the unbalancing of this equilibrium to be measured and the concentration of radical species to be estimated.

The existence of an ultraviolet light-induced dynamic equilibrium between the concentrations of NO, $NO_2$, and $O_3$ in photochemical smog was recognized very early in the study of the mechanism of photochemical smog formation.

The two gases NO and $O_3$ react very rapidly to produce $NO_2$ and $O_2$ and cannot coexist in the dark for more than a few seconds, even at low concentrations. However, in the presence of uv light, $NO_2$ is continually photolyzed to regenerate $O_3$ and thus it is possible to have a low level of $O_3$ in equilibrium with a high level of NO or vice versa. In the past, with the air pollution monitoring instruments available, it was not possible to measure a meaningful value of the concentration of the lesser of these two species. With the advent of rapid, accurate chemiluminescence NO and $O_3$ measurement devices, these measurements can now be made. Reported here are determinations of the extent to which the photostationary equilibrium holds for several hydrocarbons irradiated with NO in an environmental chamber.

### *Experimental*

The environmental chamber used was an 1100-ft$^3$ glass-walled room enclosing 72 fluorescent black lights in two banks of 36 each. Black lights emit radiation in the interval 300 to 400 nm which simulates the portion of the solar

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spectrum effective in photolyzing $NO_2$. Ozone was formed at a slow rate in the environmental chamber even after it was purged with air low in reactive hydrocarbons and oxides of nitrogen. Thus it is not well suited to the study of hydrocarbons of low reactivity. It was deemed acceptable, however, for the work described in this report, which is essentially a verification of photoequilibrium levels of $O_3$, NO, and $NO_2$. A gas purification system (consisting of a permanganate bed, activated carbon bed, and a filter) lowered background levels of $NO_x$ and reactive hydrocarbons in the chamber. The degree of reduction is dependent upon the day to day cleanliness of ambient air used in filling the chamber. In general the background $NO_x$ was around 0.05 ppm.

The concentrations of NO and $O_3$ were measured by separate commercial chemiluminescent air-monitoring instruments, both having a most sensitive full-scale range setting of 10 ppb. Both instruments had a response time of less than 1 sec, and the sample transit time through 15 ft of Teflon tubing was 2 sec. The accuracy of chemiluminescent air-monitoring instruments has been described by Stedman et al. (1972), who give a discussion of their use in smog studies. The exponential dilution method performed on the NO instrument showed that it was linear and accurate down to 10 ppb at which point background NO levels in the zero dilution gas interfered. The NO instrument was calibrated by addition of known amounts of NO to the 1100-ft$^3$ chamber. The instrument zero was determined by sampling gas containing ozone. (This was performed merely by turning off the chamber lights at the end of a run.) This zero was about 2 ppb higher than the zero obtained by turning off power to the lamp serving as an $O_3$ generator. The ozone instrument was zeroed in the presence of NO in the dark and calibrated by the neutral-buffered KI method used with an ozone generator. Ozone concentrations of approximately 0.5 ppm were used for this calibration. The NO instrument also measured $NO_2$ by passing the sample gas through a hot stainless steel catalytic converter. This reading is a measure of total oxides of nitrogen and also includes some contribution from organic and inorganic nitrates if present. Thus, the $NO_2$ measurement has some uncertainty late in a chamber run after appreciable $NO_2$ has been oxidized to nitrates. The concentration of $NO_2$ was also measured with a continuous Saltzman analyzer. This instrument does not present real time data. However, for gradual changes in concentration the data can be corrected by subtracting 20 min from the time of each reading. This compensates for the time lag of the instrument while ignoring the integration effect.

The sample line extended to the middle of the chamber between the two banks of lamps. The sample transit time in the dark tubing was only 2 sec, but ignoring the depletion of NO or $O_3$ by their mutual reaction even for this short period could lead to errors as high as 30% in the measured concentrations. It is a simple matter, however, to correct the observed reading to the actual reading at the beginning of the sample line. When we use the known rate of the NO + $O_3$ reaction (Table I), it can be shown that

$$[NO]_i = [NO]_o \exp([O_3]_o k_3 t) \quad (1)$$

$$[O_3]_i = [O_3]_o \exp([NO]_o k_3 t) \quad (2)$$

where $i$ refers to the initial reading at the sample probe inlet and $o$ to the observed reading. These equations are exact for cases where the concentration of the major species far exceeds that of the other species. During these periods the correction in the minor species ($O_3$ at the beginning of an experiment and NO at the end) is large while the correction in the major component is negligible. For example if $[NO] \gg [O_3]$ then $[NO]_i \approx [NO]_o$ which is the value used in the exponential of Equation 2.

During the midpoint of the run, when $[O_3] \approx [NO]$, Equations 1 and 2, while not exact, can be used since they give a correction which differs negligibly from the exact solution to the differential equation.

For example, the exact solution when $[NO]_o = [O_3]_o$ is

$$[NO]_i = [O_3]_i = \frac{[NO]_o}{1 - kt[NO]_o}$$

In these experiments the NO and $O_3$ concentrations were equal in the region $[NO]_o = [O_3]_o \approx 0.030$ ppm. For this concentration the exact solution gives $[NO]_i = 0.03093$ while Equation 1 yields $[NO]_i = 0.03092$. It is during this period of approximately equal concentration that the net error (product of the correction term for NO times the term for $O_3$) is smallest. The error is then about 3% for each species. We have used Equations 1 and 2 to calculate the reported concentrations.

These equations were checked experimentally by connecting bags of NO and $O_3$ to the monitoring instruments. These bags were first connected individually to determine their true concentrations and then connected in parallel to the instruments using a "Y" connector and 10 ft of tubing. The predicted and measured decrease in concentrations agreed within a few percent.

The internal ultraviolet lights caused the chamber gradually to heat up over a period of several hours. As the chamber heated up, the uv output of the black lights decreased in accord with their known operating characteristics. These difficulties were surmounted by using only 24 of the 72 lamps. The temperature then rose from 70–85°F in about 2.5 hr. The concurrent diminishing light intensity was monitored with a photocell sensitive from 300–400

**Table I. Chemical Reactions Considered**

| No. | Reaction | Rate Constant | Reference |
|---|---|---|---|
| 1 | $NO_2$ + uv light → NO + O | See Tables II and III | Holmes et al. (1973) |
| 2 | $O + O_2 + M \rightarrow O_3 + M$ | $2.33 \times 10^{-5}$ ppm$^{-2}$ min$^{-1}$ | Johnston (1968) |
| 3 | $NO + O_3 \rightarrow NO_2 + O_2$ | 29.5 ppm$^{-1}$ min$^{-1}$ | Johnston and Crosby (1954) |
| 4 | $RO_2 + NO \rightarrow NO_2 + RO$ | See text | |
| 5 | $O_3 + C_3H_6 \rightarrow$ initial products | 0.0134 ppm$^{-1}$ min$^{-1}$ | Johnston (1970), av value of several studies |
| 6 | $O_3$ + chamber walls → products | $2 \times 10^{-2}$ min$^{-1}$ | This work |
| 7 | $O_3 + NO_2 \rightarrow NO_3 + O_2$ | 0.106 ppm$^{-1}$ min$^{-1}$ | Johnston and Yost (1949) |
| 8 | $NO_3 + NO \rightarrow 2NO_2$ | Fast | |
| 9 | $NO_3 + NO_2 \leftrightarrows N_2O_5$ | Fast | |
| 10 | $N_2O_5 + H_2O \rightarrow 2HNO_3$ | | |
| 11 | $HNO_3 + NO \rightarrow NO_2 + HONO$ | Fast | Gray et al. (1972) |

nm. This light intensity was put on an absolute basis by a $k_1$ determination as described by Holmes et al. (1973). At the conclusion of the run a 1-mil Tedlar bag containing about 1 ppm $NO_2$ in $N_2$ was prepared. This bag was covered with a black shroud and attached to the end of the sample line in the chamber. The shroud was pulled away to initiate the $NO_2$ photolysis, terminated after about 1 min by turning off the lights. This method eliminates problems due to very nonuniform changes in light intensity if the lamps are turned on to initiate photolysis. The light transmission of the 1-mil Tedlar in the region 300–400 nm was determined to be 89%.

*Results and Discussion*

Table I lists the reactions considered in this work. The first three reactions listed comprise the most rapidly occurring reactions in smog and establish the photostationary state as described in Equation 3

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]} \quad (3)$$

For a discussion of the photo-induced equilibrium see Leighton (1961) or Stephens (1969).

For high [NO] in the early stages of photolysis the difficult to measure $O_3$ concentration can be predicted from Equation 3. Conversely, late in the photolysis the difficult-to-measure NO level can be predicted from the high $O_3$ concentration.

One uncertainity in the prediction lies in values of the rate constants $k_1$ and $k_3$. The value of $k_1$ has been discussed above and is felt to be accurate. The values of $k_3$ determined previously are compiled in Johnston et al. (1970), and we have used their recommended value of 29.5 $ppm^{-1}$ $min^{-1}$. This value yields good agreement with our own results as seen below.

The accuracy of Equation 3 for two "unreactive" systems is illustrated in Tables II and III. These experiments involved the reaction of 0.25 ppm NO with 1.0 ppm isobutane and 1.0 ppm of ethylene. The experimentally observed values of NO and $O_3$ are tabulated next to their values predicted from the photostationary equilibrium. There is very good agreement between predicted and observed concentrations for the duration of both of these runs, the difference in most cases is within ±10%. The $NO_2$ concentrations in these tables were measured with the chemiluminescent instrument and no appreciable interference from other forms of $NO_x$ (nitrates) is indicated.

Table IV and V present data from a more reactive hydrocarbon, propylene, irradiated at 0.25 and 1.0 ppm with

**Table II. Parameters for Reaction of 0.25 Ppm NO with 1.0 Ppm Isobutane**

| $t$, min | $k_1$, $min^{-1}$ | $NO_2$, ppb | $O_3$, ppb | Predicted[a] $O_3$, ppb | NO, ppb | Predicted[a] NO, ppb |
|---|---|---|---|---|---|---|
| 0 | 0 | 50 | 0 | 0 | 280 | |
| 40 | 0.139 | 80 | 1.45 | 1.51 | 250 | |
| 80 | 0.125 | 130 | 4.23 | 2.82 | 195 | |
| 120 | 0.117 | 200 | 7.95 | 6.14 | 129 | |
| 160 | 0.114 | 253 | 13.7 | 12.7 | 77.0 | |
| 200 | 0.114 | 290 | 27.2 | 28.0 | 40.2 | |
| 240 | 0.112 | 300 | 52.0 | | 22.4 | 21.9 |
| 280 | 0.112 | 300 | 76.0 | | 14.8 | 15.0 |
| 320 | 0.112 | 300 | 98.0 | | 10.2 | 11.6 |

[a] Equation 3.

**Table III. Parameters for Reaction of 0.25 Ppm NO with 1.0 Ppm Ethylene**

| $t$, min | $k_1$, $min^{-1}$ | $NO_2$, ppb | $O_3$, ppb | Predicted[a] $O_3$, ppb | NO, ppb | Predicted[a] NO, ppb |
|---|---|---|---|---|---|---|
| 0 | 0 | 38 | 0 | 0 | 235 | |
| 20 | 0.143 | 82 | 1.71 | 2.0 | 196 | |
| 40 | 0.140 | 125 | 3.58 | 3.9 | 153 | |
| 60 | 0.129 | 175 | 7.55 | 7.4 | 103 | |
| 80 | 0.127 | 220 | 14.8 | 15.8 | 60 | |
| 100 | 0.124 | 249 | 32.4 | | 30 | 32.3 |
| 120 | 0.120 | 263 | 62.0 | | 15.5 | 17.3 |

[a] Equation 3.

**Table IV. Parameters for Reaction of 0.25 Ppm NO with 0.25 Ppm Propylene**

| $t$, min | $k_1$, $min^{-1}$ | $NO_2$,[a] ppb | $O_3$, ppb | Predicted[b] $O_3$, ppb | NO, ppb | Predicted[b] NO, ppb |
|---|---|---|---|---|---|---|
| 0 | 0 | 40 | 0 | 0 | 250 | |
| 20 | 0.139 | 84 | 1.9 | 1.9 | 206 | |
| 40 | 0.123 | 127 | 3.6 | 3.3 | 163 | |
| 60 | 0.113 | 174 | 6.8 | 5.7 | 116 | |
| 80 | 0.110 | 216 | 12.1 | 10.9 | 74.0 | |
| 100 | 0.110 | 250 | 21.8 | 22.2 | 42.0 | |
| 120 | 0.108 | 265 | 41.0 | | 25.0 | 23.6 |
| 140 | 0.107 | 275 | 63.6 | | 15.5 | 15.7 |
| 160 | 0.106 | 280 | 87.3 | | 11.0 | 11.5 |
| 180 | 0.105 | 280 | 106 | | 9.0 | 9.4 |
| 200 | 0.105 | (261) | 126 | | 6.5 | 7.4 |
| 250 | 0.103 | (245) | 159 | | 4.6 | 5.4 |

[a] Parentheses indicate Saltzman data. [b] Equation 3.

**Table V. Parameters for Reaction of 0.25 Ppm NO With 1.0 Ppm Propylene**

| $t$, min | $k_1$, $min^{-1}$ | $C_3H_6$, ppb | $NO_2$,[a] ppb | $O_3$, ppb | Predicted $O_3$, ppb | NO, ppb | Predicted[b] NO, ppb | $k_4RO_2$,[c] $min^{-1}$ | $k_4RO_2$,[d] $min^{-1}$ | $k_4RO_2$[e], $min^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | | 950 | 35 | 0 | 0 | 240 | | | | |
| 10 | 0.161 | | 75 | 1.6 | 2.0 | 205 | | | | |
| 20 | 0.154 | | 113 | 3.2 | 3.5 | 167 | | | | |
| 30 | 0.145 | 890 | 165 | 6.1 | 6.5 | 125 | | | | |
| 40 | 0.139 | | 205 | 10.4 | 11.2 | 86 | | | | |
| 50 | 0.139 | | ... | 23.1 | ... | 45 | | | | |
| 60 | 0.139 | 820 | ... | 49.0 | | 20 | ... | | | |
| 70 | 0.132 | | ... | 88.0 | | 9.6 | ... | | | |
| 80 | 0.129 | | (220) | 135 | | 5.4 | 7.1 | 1.3 | 1.6 | 0.6 |
| 90 | 0.129 | 710 | (200) | 175 | | 3.7 | 5.0 | 1.8 | 2.5 | 1.0 |
| 100 | 0.125 | | (190) | 205 | | 2.9 | 3.9 | 2.2 | 2.9 | 1.4 |
| 150 | 0.120 | 450 | (134) | 253 | | 1.3 | 2.2 | 4.5 | 4.3 | 2.8 |

[a] Parentheses indicate Saltzmann data. [b] Equation 3. [c] Equation 5. [d] Equation 7. [e] Equation 8.

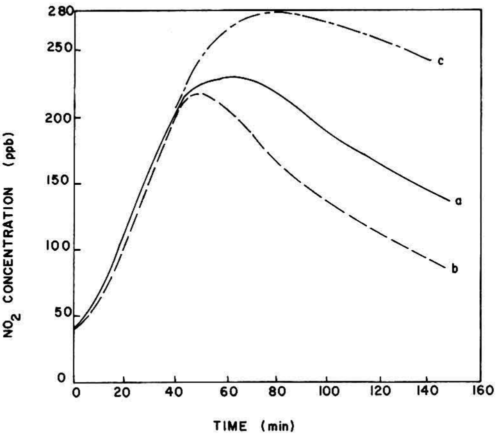

**Figure 1.** Discrepancy in $NO_2$ concentration data

Curves refer to the run given in Table V: (*a*) Saltzman data, (*b*) $NO_2$ concentration predicted from photostationary equation (Equation 3), (*c*) chemiluminescence data obtained with stainless steel converter

0.25 ppm of NO. For the lower propylene concentration (Table IV) there is again excellent agreement between measured and predicted $O_3$ and NO concentrations. The last two entries for $NO_2$ concentration are taken from the Saltzman data because the chemiluminescent instrument is probably in error. The $NO_2$ reading obtained with the catalytic converter probably contains a contribution from PAN which will cause its value to be high.

This discrepancy is illustrated more clearly in the $NO_2$ data for the more reactive system of 1 ppm propylene (Figure 1). Three values of the $NO_2$ concentration are plotted. These are the Saltzman and chemiluminescent data and values of the $NO_2$ concentration predicted from Equation 3 using the measured concentrations of NO and $O_3$. The three curves are in good agreement in the rising portion. This indicates three things: The time correction in the Saltzman data is approximately correct, there are no appreciable interferences in the chemiluminescent determination, and the photostationary equilibrium is valid. This latter conclusion is expected on the basis of data in Tables II, III, and IV.

After about 50 min of irradiation, however, all three curves diverge. The time of 50 min is approximately when the ozone concentration exceeds the NO concentration (Table IV) and a rapid increase in the net ozone formation rate occurs. This time corresponds to the traditional appearance of measurable ozone using a wet chemical instrument and to PAN appearance (see data of Altshuller et al. 1967). The chemiluminescent readings continue to increase until they reach a maximum which is approximately equal to the initial total $NO_x$. Thus, the catalytic converter apparently reduces nitrate, principally PAN, as well as $NO_2$ with 100% efficiency. In other words, total $NO_x$ includes PAN. Saltzman readings decline in the latter part of the run in agreement with the reported behavior of this system (Altshuller et al. 1967) indicating conversion of $NO_2$ to PAN or other organic or inorganic nitrates. There is a considerable discrepancy between the Saltzman data and the value of $[NO_2]$ predicted from the photostationary equilibrium, however. Although the uncertainty in the Saltzman data must be considered, the agreement in the first half of the run followed by a consistent disagreement of about 50 ppb later in the run is larger than the experimental error can explain and is therefore meaningful. Thus the photostationary equilibrium, Equation 3, appears to break down in the latter stages of the reaction causing $NO/NO_2/O_3$ concentrations to deviate from photoequilibrium levels.

Deviations from photoequilibrium levels, of course, have been anticipated by many workers in the field, although their actual measurement has not been made in the past. These deviations may be explained by considering Reaction 4, as well as Reactions 1, 2, and 3 in Table I.

Writing the equation for interconversion of NO and $NO_2$,

$$\frac{d[NO]}{dt} = k_1[NO_2] - k_3[NO][O_3] - k_4[RO_2][NO] \quad (4)$$

and making the steady state assumption for [NO] (certainly valid at the end of a run when [NO] is changing very slowly), we obtain

$$k_4[RO_2] = k_1\frac{[NO_2]}{[NO]} - k_3[O_3] \quad (5)$$

The right-hand side of this equation is simply the precursor of the photostationary equilibrium, Equation 3, and will be equal to zero if the photoequilibrium is valid. In other words, the term $k_4[RO_2]$ will be negligibly small. However, if this term becomes large enough to perturb the photostationary state, then its value may be calculated from Equation 5. This is actually the case at the end of the run made with 1 ppm propylene. Calculated values of the term $k_4[RO_2]$ are shown in Table V.

This analysis can be carried a step further by considering the first seven reactions in Table I. Reactions 1, 2, 3, 5, 6, and 7 attempt to account for all ozone reactions fast enough to be important. Writing the differential equation for ozone, we obtain

$$\frac{d[O_3]}{dt} = k_1[NO_2] - k_3[NO][O_3] - k_5[O_3][C_3H_6] - k_7[O_3][NO_2] - k_6[O_3] \quad (6)$$

By subtracting Equations 4 and 6 and rearranging, we can obtain an independent measure of the term $k_4[RO_2]$:

$$k_4[RO_2] = \frac{1}{[NO]}\left\{\frac{d[O_3]}{dt} - \frac{d[NO]}{dt} + k_5[O_3][C_3H_6] + k_7[O_3][NO_2] + k_6[O_3]\right\} \quad (7)$$

The values calculated from Equation 7 are also tabulated in Table V.

This is a less certain method (relative to Equation 5) since it involves rate constants known with less certainty and also since Equation 6 may conceivably ignore an important $O_3$ formation or destruction reaction. The agreement in Table V between Equations 5 and 7 is quite good, however.

This agreement is significant, since it tells us that we probably have accounted for all important $O_3$ reaction processes. One process which has been suggested in the past is $RO_2 + O_2 \rightarrow O_3 + RO$. This reaction is usually rejected on the grounds that it must be endothermic, but it is still invoked in the interpretation of some smog processes (see for instance Ripperton and Lillian, 1971). If some other important process of ozone generation were occurring, then this would result in Equation 7 yielding a larger value of $k_4[RO_2]$ than Equation 5. The actual differences in Table V, however, are not significant in terms of uncertainties in $k_5$ and $k_7$.

Another way of saying the same thing is that there is reasonably good agreement between the experimentally observed value of $d[O_3]/dt$ and the value predicted from Equation 6.

The generalized term $k_4[RO_2]$ does not imply that alkyl peroxy radicals are the only NO to $NO_2$ conversion species. Rather, this term is simply the sum of all conversion species (other than $O_3$) times their respective rate constants.

In fact, two conversion processes omitted from consideration until now are comprised in Reactions 7 and 8, and Reactions 7, 9, 10, and 11. These processes make a small contribution except late in the reaction, and they do not "drive" the ozone buildup since each consumes a molecule of $O_3$ to convert NO to $NO_2$.

An upper limit for the contribution of these two processes to the term $k_4[RO_2]$ may be calculated if we assume that all $NO_3$ radicals eventually convert NO to $NO_2$. Equating the rate of $NO_3$ formation to the rate of NO conversion by $NO_3$ or its reaction products and dividing by [NO], we obtain

$$k_8[NO_3] + k_{11}[HNO_3] = \frac{k_7[O_3][NO_2]}{[NO]} \qquad (8)$$

Values of this term are also listed in Table V and are seen to make an appreciable contribution to the term $k_4[RO_2]$ calculated using Equation 5. These values are probably an overestimation since $NO_3$ does have other removal processes in addition to its reaction with NO or $NO_2$.

## *Conclusions*

In this study, photoequilibrium levels of $O_3$, NO, and $NO_2$ have prevailed during most or all of a number of photochemical smog reactions employing hydrocarbons of moderate-to-low reactivity. This fact has been anticipated by a number of workers in the field of photochemical air pollution although the extent over which equilibrium would hold has not been demonstrated in the past. Conversely, light intensity measurements using the $k_1$ or $k_d$ method of Tuesday have been shown to be in good agreement with $k_1$ values calculated from Equation 3. In fact, Equation 3 coupled with the proper monitoring instruments can probably obviate the necessity of making an independent $k_1$ determination by the $NO_2$ photolysis method. The most accurate time to calculate $k_1$ from Equation 3 would be when the $O_3$ and NO concentrations are equal, since this is when the product of the two needs to be corrected the least for reaction in the sample line. It is likely, furthermore, that Equation 3 will be valid this early in most smog reactions.

The validity of Equation 3 during much or all of the runs discussed does not imply that there are no $RO_2$ radicals (or their equivalent) present, but only that their concentration is small. These radical species are of great importance in photochemical air pollution since they actually drive the smog-forming reaction. They are responsible for the conversion of NO to $NO_2$ and subsequently are indirectly responsible for ozone accumulation. The key process, as discussed by many writers in the field, is the conversion of a molecule of NO to $NO_2$ without the destruction of an ozone molecule in the process. The phrase hydrocarbon reactivity as commonly used is simply a reference to the ability of a particular hydrocarbon or group of hydrocarbons to generate and maintain appreciable levels of these radical conversion species.

The magnitude of the term $k_4[RO_2]$ can be estimated late in a smog experiment by Equation 5 and this requires the accurate measurement of ppb levels of NO in the presence of high $O_3$ levels. During this portion of the experiment, the term $k_4[RO_2]$ can become appreciable, as evidenced in Table V. If a value of 1 $min^{-1}$ is taken as reasonable for the term $k_4[RO_2]$ in Table V late in the reaction, it is possible to approximate a concentration for $RO_2$ using values of $k_4$. Unfortunately experimental values of $k_4$ are largely unknown except for the case of $HO_2 + NO \rightarrow HO + NO_2$ for which an experimental value of $k_4 \approx 450$ $ppm^{-1}$ $min^{-1}$ has been established (Davis et al. 1973). Demerjian et al. (1973) have recently estimated the rate constant for $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ as 910 $ppm^{-1}$ $min^{-1}$. If $k_4$ is indeed about 800 $ppm^{-1}$ $min^{-1}$, then the concentration of "$RO_2$" radicals late in the experiment shown in Table IV will be about 0.1 ppb.

This analysis is limited by the uncertainties inherent in use of a wet chemical method (Saltzman) to measure accurate real time concentrations of $NO_2$. Figure 1 illustrates the inadequacy of the catalytic converter used in conjunction with the chemiluminescent method for $[NO_2]$ determination. Once a more precise, real time, $[NO_2]$ instrument is available, the analysis described in this paper can be applied to other reactive systems.

While Table V is not sufficient evidence to rule out the reaction $RO_2 + O_2 \rightarrow RO + O_3$ for the propylene system, it does suggest that it is at best of minor importance. Rather, the influence of radical species on rapidly converting NO to $NO_2$ is sufficient to account for the $O_3$ buildup. Measurement of low NO concentrations in other smog chamber experiments and in the atmosphere should give additional information along these lines. The common usage that chemiluminescent instruments are now achieving should clear up this and other questions and put all of smog kinetics on a much firmer ground.

One final point worthy of mention lies in the interpretation of Equation 3 describing the photostationary state. This equation gives useful information about the smog process but it does not *determine* what the ozone concentration will be late in a smog reaction. If anything, the quantity determined by Equation 3 is the very low NO concentration. The $O_3$ concentration is determined rather by the complicated chain of chemical reactions which occurred prior to its measurement, the effect of which can only be estimated by an integration process over this prior time period.

## *Acknowledgments*

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# Development of Sampling and Analytical Procedure for Determining Hexachlorobenzene and Hexachloro-1,3-butadiene in Air

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■ Chromosorb 101 efficiently trapped vapors of hexachlorobenzene (HCB) and hexachloro-1,3-butadiene (HCBD) from air at a sampling rate of 3 l./min. No loss of efficiency was noted with sampling times of up to 3 hr. Increasing the sampling rate to 10 l./min. for 1 hr decreased the efficiency by 20%. The method as described has a detection limit of 28 ng of hexachlorobenzene per cubic meter of air.

A recent episode in which the guidelines for hexachlorobenzene (HCB) in meat (0.3 ppm) was exceeded prompted an investigation into the source of the contamination. The grass in pastures around certain chemical plants was found to contain hexachlorobenzene (HCB). Air pollution was considered as one possible source of this contaminant. An efficient, portable, air-sampling device, which would yield HCB in a form amenable to subsequent analysis by electron capture gas chromatography, was needed.

The objective of this study was to develop, evaluate, and field test such a device. An on-going in-house research program designed to improve methodology for determining pesticides in air provided clues to the best approach for resolving this problem (Seiber et al., 1973).

An ethylene glycol impinger system originally described by Miles et al. (1970) and later adapted by Enos et al. (1972) was less desirable for field use than a solid adsorbent trap attached to a portable battery-powered air pump. The solid adsorbent suggested for this work (Seiber, 1973) was Chromosorb 101.

*Experimental*

**Preparation of Chromosorb 101.** Chromosorb 101 (60/80 mesh) was extracted for 4 hr using a Soxhlet apparatus charged with 5% acetone in methanol. Six washing cycles per hour proved adequate. A similar wash with hexane was repeated twice. The Chromosorb 101 was dried for 30 min at 70°C. A 1-gram portion was extracted with 20 ml of hexane by shaking in a 50-ml test tube for 20 min on a reciprocating mechanical shaker. A 4-ml aliquot of the supernatant was concentrated to 1 ml and a 5-$\mu$l. portion injected into a gas chromotograph for the purpose of establishing the background contribution from the adsorbent. Injection was made into a gas chromatograph containing a 1.5% OV-17/1.95% QF-1 column heated to 150°C and equipped with an electron capture detector. The sensitivity of the gas chromatography system was such that a 50-pg injection of HCB resulted in at least a 50% full-scale deflection with a noise level of less than 2%.

**Table I. Trapping Efficiency for HCB and HCBD on Chromosorb 101**

| No. of replicates | Air ng/m$^3$ | Sampling time and rate | Trapping efficiency, % | Range |
|---|---|---|---|---|
| | | HCB | | |
| 5 | 5560 | 1 hr, 3 lpm | 92.9 | 88.5–97.5 |
| 2 | 1666 | 1 hr, 10 lpm | 79.0 | 78.0–80.0 |
| 1 | 1110 | 1 hr, 3 lpm | 97.0 | |
| 2 | 1850 | 3 hr, 3 lpm | 91.6 | 87.4–95.7 |
| 2 | 370 | 3 hr, 3 lpm | 99.5 | 98.9–100 |
| | | HCBD | | |
| 3 | 4170 | 1 hr, 2 lpm | 100.5 | 98.0–103 |

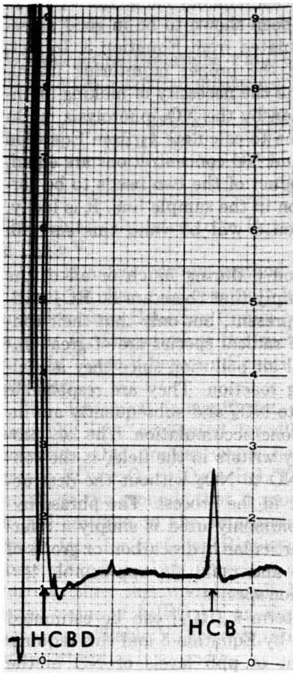

**Figure 1.** Field sample collected at rate of 2 l./min for 1 hr was equal to 900 ng HCB/m$^3$ air diluted to 40 ml

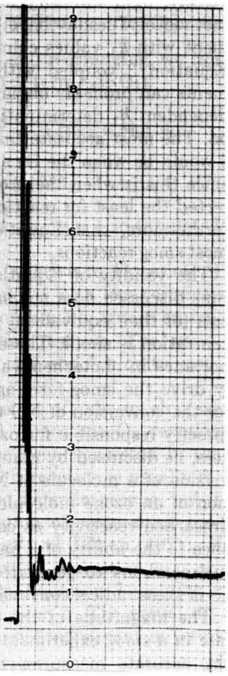

**Figure 2.** One gram Chromosorb 101 after cleanup; 20 ml concentrated to 5 ml

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**Preparation of Collection Tube.** A 4-in. length of 10-mm i.d. glass tubing was fire polished at both ends. A crimp was made about 1 in. from one end of the tube to retain a small plug of glass wool. One gram of Chromosorb 101 was placed in the tube followed by another plug of glass wool.

**Evaluation of Collection Tube.** Known amounts of HCB and hexachlorobutadiene were placed in a U tube and the U tube was connected to the collection tube. After air was drawn through the tubes at a known rate for a specified period of time the Chromosorb 101 was transferred to a test tube containing 20 ml of hexane and shaken for 20 min. Analysis was completed by injecting a 5-$\mu$l. aliquot into a gas chromatograph equipped and operated as described above.

### *Results and Discussion*

The results in Table I indicate that a high level of trapping efficiency can be obtained for vapors of HCB and HCBD. HCB was trapped efficiently at a sampling rate as high as 10 l./min (lpm).

For most purposes, a rate of 2 l./min and a sampling interval of 3 hr should be sufficient. Under these conditions and with a preliminary concentration of the extract (4 to 1), a limit of detection of 28 ng/m$^3$ of air [about 22 parts per trillion (ppt)] can easily be achieved.

HCB was stable when adsorbed on Chromosorb 101 from the vapor phase and stored at room temperature for up to 6 days. This allowed sufficient time to transport samples from the field to the laboratory.

Field evaluation of the sampling device was accomplished by obtaining samples upwind and downwind of a chemical plant manufacturing perchloroethylene. Samples were also taken around a land fill area used by the plant for disposing of waste chemicals.

An air sample taken downwind of the plant contained 990 ng HCB/m$^3$ while an upwind sample contained 915 ng/m$^3$. An air sample taken on a dustless day in the vicinity of the land fill contained 18.6 mcg/m$^3$.

HCBD was also found in the samples described above but it was not quantitated.

The identities of HCB and HCBD in the field samples were confirmed by mass spectrometry.

Figure 1 is a chromatographic tracing depicting both the HCB and HCBD as they appear in a field sample. Figure 2 is typical of the background obtained from Chromosorb 101 when it was prepared and evaluated as described in this method.

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# Rare Earth Element Composition of Atmospheric Particulates

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■ The relative and absolute rare earth element (REE) concentrations of atmospheric particulate matter are still very poorly known. The REE do not constitute an apparent health hazard, although their toxicology is not well defined. However, as a tool for determining sources and particulate formation processes, they warrant further study. Analyses for nine of the REE (sufficient to define relative distribution patterns) are reported for three air particulate samples collected in the metropolitan St. Louis area. Differences are observed that, with additional data, should prove useful in defining source materials and modes of atmospheric particulate loading.

Very few data on the rare earth element (REE) contents of air particulates are available in the literature. In addition, the available information is either of high uncertainty (Henry and Blosser, 1971) or incomplete (Gordon et al., 1973; Kay et al., 1973). The REE contents of air particulates do not present an obvious toxicological hazard at their ng/m$^3$ level but do perhaps warrant closer study for their ability as tracers and discriminators. The utility of the REE in determining the origin and formation processes of natural materials such as rocks and minerals is well documented (Haskin and Frey, 1966; Herrmann, 1970). The processes by which the REE were added to the total particulate loading of the atmosphere are certainly different from geologic processes but may be amenable to the same type of analysis based on both absolute REE contents and relative REE fractionations.

The REE behave as an essentially coherent group of elements. Relative fractionations within the group or anomalous contents of individual elements (notably Ce and Eu) are generally the most useful types of information, and they reflect directly on the formation processes and sources. To effectively view such differences it is necessary to normalize, element by element, the concentrations of the REE in a sample by those in some standard reference material. Doing so not only removes the nuclear structure effect causing the abundances of even atomic number elements to exceed those of odd atomic number elements in nature (Oddo-Harkins rule) but also yields an immediate comparison with the reference material.

The REE data (Table I and Appendix) for three air filtrate samples from the metropolitan St. Louis area have been normalized to the average REE contents of shales and are plotted versus atomic number in Figure 1. This

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choice of reference material will be justified below. Two of the samples, Soulard-0011 and GC-23, both from areas of heavy industry, have similar absolute and relative abundances. The third sample, OVLD-067, from an area dominated by light industry and residences, contains somewhat higher amounts of the REE and shows a distinctly different distribution pattern. This comparison of REE patterns and the types of urban setting is made here only as a point of information and with no intended inferences. It is certainly premature to attempt such correlations with the available data. The important fact to be noted is that significantly different fractionations of the REE (best illustrated here as differences in the ratio of heavy to light REE) are observed in the air particulates from a single metropolitan area.

The types of distribution patterns observed in the air particulate samples are perhaps most meaningful when compared with the average REE composition of sediments and sedimentary rocks, the most common materials of the earth's surface. For this purpose we have selected the average REE composition of 40 North American shales (Haskin et al., 1968) as the reference material. The REE content of these shales is very similar to that of the crustal abundance (Wedepohl, 1968) used by Gordon et al. (1973) for normalizing other elemental abundances in the atmosphere, but the shale data are more complete for the REE. The REE composition of shales should be fairly representative of natural sources of particulate matter such as soils and sedimentary rocks (Haskin and Frey, 1966). Absolute values, however, may be significantly different. The average REE content of shale should be especially representative of the rock and soil cover in metropolitan St. Louis, a terrain composed almost exclusively of residual soils, loess, and sedimentary rocks.

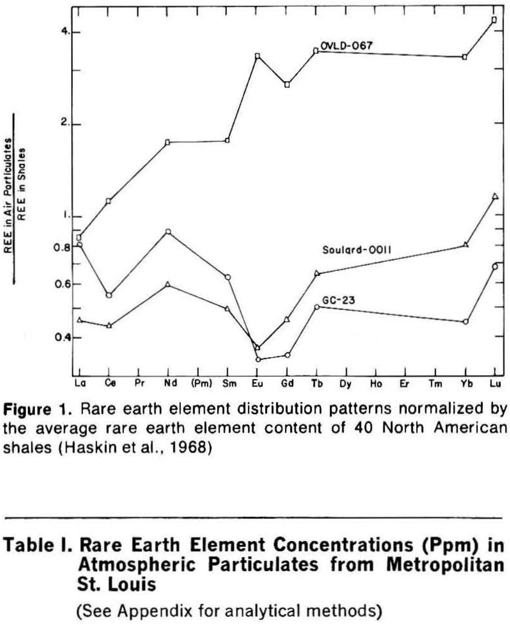

**Figure 1.** Rare earth element distribution patterns normalized by the average rare earth element content of 40 North American shales (Haskin et al., 1968)

**Table I. Rare Earth Element Concentrations (Ppm) in Atmospheric Particulates from Metropolitan St. Louis**

(See Appendix for analytical methods)

| Element | GC-23, Granite City, Ill. | Soulard-0011, St. Louis City | OVLD-067, Overland, Mo. |
|---|---|---|---|
| La | 25.9 ± 0.9[a] | 14.6 ± 0.8 | 27 ± 1 |
| Ce | 39.9 ± 0.9 | 32 ± 1 | 82 ± 2 |
| Nd | 29 ± 2 | 20 ± 2 | 58 ± 3 |
| Sm | 3.59 ± 0.06 | 2.83 ± 0.07 | 10.1 ± 0.1 |
| Eu | 0.42 ± 0.04 | 0.46 ± 0.06 | 4.1 ± 0.2 |
| Gd | 1.8 ± 1.2 | 2.4 ± 1.4 | 14 ± 3 |
| Tb | 0.43 ± 0.06 | 0.55 ± 0.08 | 2.9 ± 0.2 |
| Yb | 1.4 ± 0.4 | 2.5 ± 0.4 | 10.2 ± 0.8 |
| Lu | 0.33 ± 0.04 | 0.55 ± 0.03 | 2.07 ± 0.08 |
| ΣREE[b] | 113 | 87 | 257 |
| Air volume sampled, $m^3$ | 1476 | 851 | 1732 |
| Wt particulates collected, grams | 0.208 | 0.146 | 0.214 |

[a] Stated errors are one standard deviation based on counting statistics.

[b] Total REE content, La–Lu, including estimates for elements not determined.

In general, we would expect the REE in air particulates derived entirely from natural sources (and perhaps those derived from the burning of coal), when normalized as in Figure 1, to yield a horizontal line, but not necessarily at 1.0. Distribution patterns deviating significantly from the horizontal, such as the OVLD-067 sample, suggest contributions from artificial sources. It is too early to speculate about the possible causes for this large enrichment of the heavy REE (or possibly the depletion of the light REE) relative to the assumed natural source materials. However, it is difficult to explain as resulting from natural processes. On the other hand, "enrichment factors" for individual elements in atmospheric particulates led Gordon et al. (1973) to conclude that for the four REE determined there was no significant enrichment or depletion relative to that expected for source materials having a crustal-type elemental composition.

Further study of the distribution of the REE in air particulates may provide at least a partial solution to the problem of distinguishing natural sources from man-made sources of air pollutants. The REE have limited commercial or industrial uses at present, and each generally would have its own characteristic distribution pattern (or signature). In addition, it should be possible to characterize particulate stack emissions resulting from the combustion of natural fuels and particulate matter from wind erosion of rocks and soils. However, much more work on the REE is needed for them to become an effective tool. It would be desirable, for example, to study the REE contents in coal and the differences in REE distribution patterns, if any, in particulates emitted during its combustion. The present study, which presents data for only three metropolitan St. Louis air particulate samples, lacks such necessary background information. Continuing work in this direction on a complete set of previously collected samples, we hope, will prove as useful as these first data suggest.

### *Acknowledgment*

We wish to thank the crew of the University of Missouri Research Reactor for providing the neutron irradiations and the Department of Earth Sciences at Washington University for the use of its counting facilities.

## APPENDIX

### *Analytical Methods*

Samples were collected over a 24-hr period on 8 × 10-in. Whatman 41 filter paper using a high-volume air sampler. Analyses were performed by neutron activation analysis using a postirradiation chemical separation of the REE and high resolution, Ge(Li), counting (Potts et al., 1973). Blank values obtained on the Whatman 41 filter paper were consistently negligible.

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# Improvements in Colorimetric Analysis of Chlorine and Hydrogen Fluoride by Syringe-Sampling Technique

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■ The syringe-sampling technique for the analysis of reactive gases in air has been improved. The *o*-tolidine method for free $Cl_2$ has been extended to 300 ppm for stack gas analysis. The lanthanum-alizarin-complexan method for HF has been adapted to the syringe procedure over the range of 0.3–70 ppm. The relative analysis errors are below 4.2 and 1.6%, respectively.

The syringe-sampling technique of Meador and Bethea (1970) has been extended to the colorimetric analysis of high concentrations of $Cl_2$ in stack samples. Additional work has also led to a change in the colorimetric procedure used for the analysis of trace quantities of HF in both ambient and stack samples.

## *Experimental*

The experimental apparatus used to prepare the calibration samples by the permeation tube technique was as described in the *Federal Register* (U.S. Environmental Protection Agency, 1971). Oil-free, breathable grade air containing no measurable amounts of any reactive gas was used as supplied in commercial compressed air cylinders. The permeation rates of the $Cl_2$ and HF were determined gravimetrically after the system had reached thermal equilibrium at 25 ± 0.17°C.

**Chlorine.** At concentrations above approximately 100 ppm $Cl_2$, the working *o*-tolidine solution (0.005 g/l., Meador and Bethea, 1970) was unusable. Under those conditions, the orange color formed by the reaction between $Cl_2$ and the *o*-tolidine became immediately pronounced and then faded completely within 5–10 min. To avoid the color bleaching, 3 ml of the stock *o*-tolidine solution (1.00 g/l.) were drawn into 50-ml disposable polypropylene syringes (Becton, Dickinson, and Co., No. 850L/S) fitted with disposable stainless steel needles with polypropylene hubs (Becton, Dickinson, and Co., No. 1000). Sample air (47 ml) was then drawn into the syringe from the permeation tube apparatus at a rate of 2 ml/sec. Absorption of the $Cl_2$ was complete in 5 min of gentle hand shaking. The developed reagent was then expelled into a 1-cm i.d. cuvette and read in a colorimeter (Bausch and Lomb, Spectronic 20) at 450 nm against unexposed reagent as the 100% T reference. The cuvettes used were matched to ±0.5% T.

The calibration was carried out for 50–350 ppm. $Cl_2$ corresponding to a color range of deep orange to burnt siena (corresponding to 23–4% T). The colors so formed were stable for 2 hr. The calibration curve for the data (points taken at least in triplicate) showed Beer's law to be followed for 50–300 ppm $Cl_2$. The relative analysis error was between 3.34 and 4.18% over this concentration range.

Two cautions must be observed with this technique. Unless the syringes have been in semicontinuous use, they require overnight conditioning with several thousand ppm $Cl_2$ to obtain reproducible results. This conditioning step is required for any syringes that have not been used for stack sampling for an 8-hr period. Preconditioning of the syringes is necessary to avoid surface absorption of the reactive gas on the syringe wall. If this is not done, the first few samples (as many as 3) usually showed chlorine concentrations below those actually present.

As glass and plastic syringes from several different manufacturers had been previously evaluated (Gully et al., 1969) for their effect on reagent stability, extensive reevaluations were not necessary for the present work. The glass syringes consistently gave poorer reproducibility than plastic syringes in our previous work and were thus not retested. The polypropylene syringes described above gave the most reproducible results of the three varieties checked, and were therefore used throughout this research.

The second precaution to be observed is the requirement for preventing ghost effects between samples. This is especially important when the concentration in subsequent samples is expected to be lower than that of previous samples. The syringes must be rinsed three times with 4 ml of unexposed stock solution between samples to obtain best results.

**Hydrogen Fluoride.** The lanthanum-alizarin-complexan procedure of Belcher and West (1961a,b) was investigated for adaptation to the syringe sampling technique. The initial evaluation consisted of triplicate observation of various points on a standard aqueous NaF calibration curve prepared to be equivalent to 2.0–70 ppm fluoride in a 46-ml gas sample according to the directions of Gully et al., (1969).

In the evaluation of this procedure, a commercially prepared reagent (Amadec-F, Burdick and Jackson Laboratories, Inc., 1966, 1967) was used. The procedure was that recommended by the manufacturer with the following exception: The solvent used was a 60% (v/v) solution of 1,4-dioxane in demineralized, deionized (DMDI) water to form a solution containing 100 mg of Amadec-F per ml of solution. This corresponds to 1.0 mM each of total acetate and the lanthanum complexan chelate. This solvent gave considerably more sensitive results than the 60% (v/v) isopropanol, diethyl ether, methanol, ethanol, acetonitrile, or acetone solutions recommended by the manufacturer.

The most sensitive and reproducible results were obtained when 1 ml of the Amadec-F concentrate was added to 4 ml of the fluoride standard. The calibration was carried out using matched (±0.5% T) 1-cm i.d. cuvettes and read at 620 nm against an unexposed reagent as the 100% T reference.

The preliminary experimental data showed that after a color development time of 30 min, the depth of color became stable and remained so for 16 hr, thus confirming the observations of Yamamura et al. (1962). Further experimental work showed that solutions higher in fluoride content stabilize in shorter times after exposure as originally noted by Belcher and West (1961a). As examples, the % T decreased hyperbolically from 84 to 65 over 28.5 min at 10 ppm fluoride, from 57 to 26.4 over a 24.5-min period at 30 ppm fluoride, and from 28 to 10 over a 21-min period at 60 ppm fluoride. Thus, a minimum color development time of 30 min was selected for use.

When equivalent pairs of exposed reagent were subjected to light stability tests, no difference was noted. The rate and degree of color change as measured by % T decrease were the same for light shielded samples as for those exposed to laboratory light levels. This indicated that diffuse light (indirect natural light or fluorescent) has no effect on the stability of the exposed fluoride reagent.

In adapting this procedure to the analysis of airborne HF, 4 ml of DMDI water were drawn into properly preconditioned (about 150 ppm HF for 8 hr) 50-ml polypropylene syringes and used as the absorbing medium. Sample gas (46 ml prepared by the permeation tube technique to cover the range of 0.1–100 ppm HF) was drawn into vertically oriented syringes at the rate of 2 ml/sec. Following gentle hand shaking for 2 min, the resulting solutions were expelled into cuvettes and 1 ml of the Amadec-F concentrate was added followed by thorough mixing. The fluoride concentration was plotted against the % T after the 30-min color development time had elapsed. The data so obtained show Beer's law to be followed over the range of 1–35 ppm fluoride (corresponding to 97–20% T). The lower detection limit was 0.3 ppm fluoride. The upper reliable limit of calibration was 70 ppm fluoride. The relative analysis error for triplicate analysis of nine equally spaced points over this range was consistently below 1.52%.

As an alternate to the permeation tube technique, calibration with standard NaF solution may be used. To ten 25-ml volumetric flasks, add graduated amounts (1 ml, 2 ml, 3 ml, . . . , 10 ml) of $6.417 \times 10^{-5} M$ NaF solution. Dilute each flask to the mark with DMDI water. Add 1 ml of the Amadec-F test reagent to 4 ml of the calibration solution in a clean 1-cm cuvette and mix well by pouring back and forth into another clean cuvette. The first point is equivalent to 5 ppm HF in air as measured with a 46-ml syringe air sample. The last point is equivalent to 50 ppm. Calibration points should be determined in triplicate. The relative analysis error which may be expected over the 5–50 ppm range is between 1.4 and 2.06%.

Any syringes not used for calibrations or ambient air sampling for a period of 8 hr should be reconditioned prior to use.

This adaptation of the lanthanum–alizarin–complexan method to the syringe-sampling procedure for airborne fluoride provides a greatly extended useful range with a fivefold increase in sensitivity over the ferric sulfosalicylate fluoride bleaching method used by Meador and Bethea (1970).

### *Acknowledgment*

The assistance of R. M. Garvert in the preliminary fluoride experiments is appreciated.

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# Further Development of a Generalized Kinetic Mechanism for Photochemical Smog—Addendum

**T. A. Hecht, J. H. Seinfeld, and M. C. Dodge**

For those readers who might wish to reproduce the simulations reported in the article which appeared in *Environmental Science and Technology,* Vol. 8, No. 4, pages 327–39, we present here some additional data.

In carrying out chemical analyses of reactants and products, large volumes of gas were drawn from the chamber during an experiment. Removal of such large samples for analysis was necessary to obtain accurate determinations of contaminant concentrations. A volume of clean air, equal in volume to the amount of gas removed for sampling, was added to the chamber to maintain the total chamber pressure at 1 atm. To determine the amount of dilution, ethane, a hydrocarbon which is virtually unreactive in photochemical smog, was added to the reactant mix as a tracer gas. If ethane is assumed to be chemically inert, its loss from the chamber can be attributed entirely to sampling and dilution, carried out at an average rate given by $-dc/dt = kc$. The "rate constant" for the reaction is then $k = [2.3 \log(c_o/c_f)]/(t_f - t_o)$, where $o$ and $f$ denote the beginning and ending times of the irradiation. The average dilution rate constants for the experiments used for validation were:

| EPA run | $k \times 10^4$ (min$^{-1}$) | EPA run | $k \times 10^4$ (min$^{-1}$) |
|---|---|---|---|
| 306 | 7.5 | 307 | 9.5 |
| 314 | 8.5 | 333 | 10.0 |
| 345 | 7.5 | 348 | 7.9 |
| 318 | 8.2 | 349 | 9.3 |
| 325 | 8.5 | 352 | 9.5 |
| 329 | 8.9 | 457 | 6.9 |
| 459 | 4.8 | | |

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## ADDENDUM

**Further development of generalized kinetic mechanism for photochemical smog** 588

**T. A. Hecht, J. H. Seinfeld, and M. C. Dodge**

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