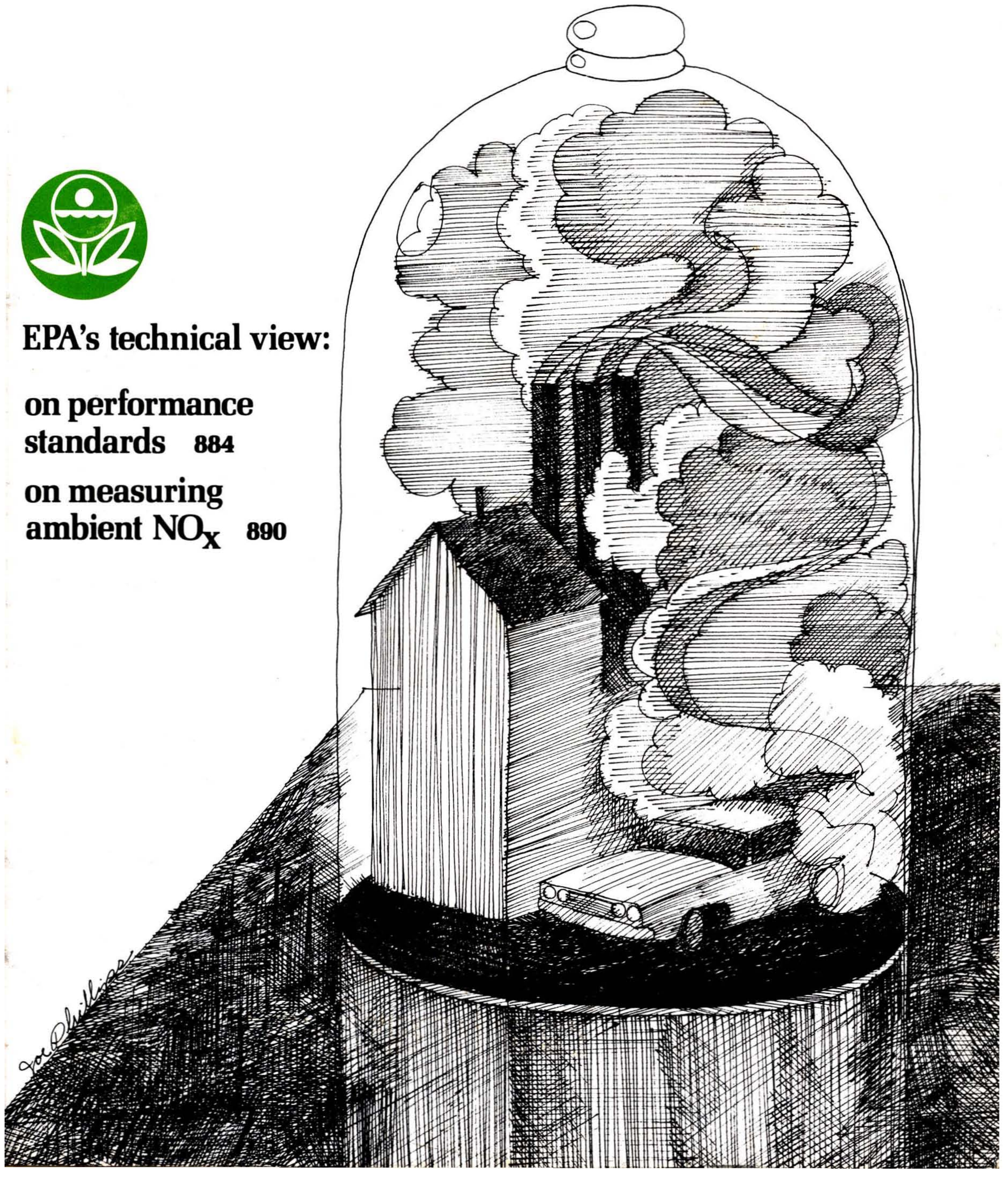
Environmental
Science & Technology

✓OCTOBER 1972

EPA's technical view:

on performance standards 884

on measuring ambient NO_x 890

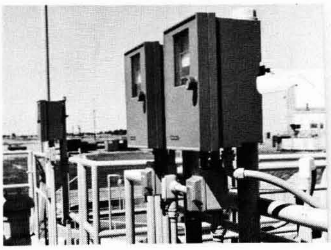


WATER AND WASTE CONTROL NEWS

Air Base Waste Controls Installed

McClellan Air Force Base (California) recently started up its new industrial waste treatment facility under centralized control by a Honeywell automation system.

McClellan is a key base in the Air Force Logistic Command network. A "city" of more than 24,000 persons, its large service and repair shops provide worldwide day and night logistic support for combat jets like the F-111, F-100, and F-105. The 1.2 - 2.4 MGD flow of wastewater from the shop complex contains free and emulsified oils, chrome and acid-bearing solutions, and heavy metal "dragout" from plating operations.



Model 54 water management analyzer instruments measure pH and ORP values in neutralizing and chrome reduction tanks at McClellan Air Force Base industrial waste treatment facility and transmit signals to central control panel. Design of Model 54 instruments suits them for outdoor application, with minimum maintenance attention.

Oils are separated, heavy metals precipitated, chrome reduced, and acids neutralized in the treatment plant. The effluent from the facility is further processed through aeration tanks and a chlorine contact stage before discharge into Magpie Creek which leads into the Sacramento River.

System instrumentation — including the latest Class 54 Analyzer-Transmitters and *VutroniK* electric recording and indicating controllers — was furnished and installed by Honeywell and started up with technical assistance by Honeywell. The facility and control system was designed by the San Francisco consulting firm of Kennedy Engineers.

Improved Parts Service for Honeywell Customers

Industrial Division's new parts depot at Indianapolis, Ind., is now ready for business to serve needs of customers with 24-48 hour delivery of parts, charts, thermocouples, wire, and stock instruments. 20,000 square feet of floor space provide storage for approximately 12,000 items. The depot is located in Park Fletcher Industrial Park within a short distance of the Indianapolis airport and major through highways.

The Indianapolis depot complements Fort Washington as a centralized source of spare parts for the U.S.

Inspect our Pollution Control Capabilities at Atlanta Conference

At the Water Pollution Control Federation Conference, to be held at the Municipal Auditorium in Atlanta, Ga., October 8 - 12, you can get a good feel for the overall water and wastes control capabilities of Honeywell's Industrial Division.

Visit booths 329-331-333. Among the many products on display will be: field-mountable analyzer-transmitters for pH, ORP, conductivity and DO; chlorinator; chemical feeder; residual chlorine analyzer; and miniature, intermediate-size and conventional-size instruments.

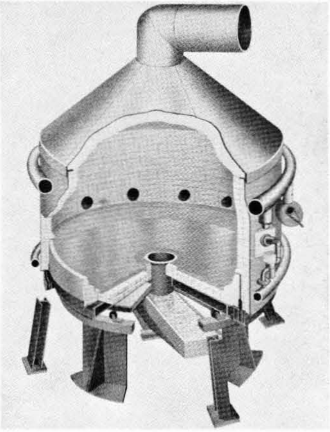
Honeywell
The Automation Company
INDUSTRIAL DIVISION, M 436,
FORT WASHINGTON, PA. 19034

Control Instrumentation since 1860

Circle No. 10 on Readers' Service Card

Old Tires Fuel New Furnace

A new, smokeless, odorless Tire Destruction Furnace, controlled by Honeywell instrumentation, will use old tires as fuel to generate heat feeding a steam boiler for new tire production at The Goodyear Tire & Rubber Company plant in Jackson, Mich.



Cross-section diagram shows basic configuration of Lucas Tire Destruction Furnace of the type soon to go into operation to generate steam power at The Goodyear Tire & Rubber Company plant in Jackson, Mich. First of its kind in the U. S., the unit will consume about 3,000 old tires a day.

The unit, to be built and installed by Lucas American Recyclers, Inc., of South San Francisco, will burn whole tires without any shredding to a sterile, inert ash. Tires are fed by conveyor to the outer edge of the furnace's rotating hearth. From there they travel in a spiral to the center where the intense heat—up to 2400 degrees Fahrenheit—is sufficient to oxidize even the wire bead.

VutroniK miniature indicating proportional controllers automatically regulate furnace temperatures to achieve optimum combustion conditions.

Completion date for the project, first of its kind in the U. S., is scheduled for late summer. Several Lucas Tire Destruction Furnaces are being operated successfully in England.

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contents

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Features

Interview

Outlook

Departments

Current research

Corona discharge oxidation of sulfur dioxide 895

M. J. Matteson, H. L. Stringer, and W. L. Busbee

The presence of sulfuric acid mist seriously lowers the collection efficiency of electrostatic precipitators. To study the conversion of sulfur dioxide to acid mist, sulfur dioxide (50–300 ppm) in a flowing humid air mixture was exposed to a corona discharge in a wire-to-cylinder reactor. Optimum reaction rates occurred at 70% r.h. and more than 15% oxygen concentration.

Mercury levels in muscle tissues of preserved museum fish 901

R. J. Evans, J. D. Bails, and F. M. D'Itri

The 1970–71 mercury levels in fish from two study areas in Canada were found to average more than preserved museum specimens in the same categories taken from the same area. The present levels were compared with 57 preserved fish including 26 different species specimens in the Great Lakes (Lake St. Clair–Western Lake Erie region) between the years 1920–1965. Only five fish (three muskellunges in 1939, and two sea lampreys in 1938) were found to contain mercury levels in excess of 0.5 ppm, the current FDA action level.

Separation of oil dispersions from water by fibrous bed coalescence 905

W. M. Langdon, P. P. Naik, and D. T. Wasan

A coalescer/separator unit with a 1-ft^2 active area has been designed for removing dispersed oil from water. It was tested on both a synthetic stream and on an actual pollutant stream. The controlling parameter for a practical unit appears to be the life of the bed; pressure builds up in the unit owing to the accumulation of oil in the bed.

Dissipation of pesticides from soil by volatilization of degradation products. I. Lindane and DDT 910

M. M. Cliath and W. F. Spencer

Volatilization of degradation products can be a major pathway for loss of some chlorinated hydrocarbon insecticides from the soil. The primary degradation products of lindane and DDT have much higher vapor pressures than the parent compound; consequently, they have a greater volatilization rate.

Fate of DDT in Severn estuary sediments 914

E. S. Albone, G. Eglinton, N. C. Evans, J. M. Hunter, and M. M. Rhead

DDT is degraded more slowly in actual estuarine sediments (Severn estuary which drains one sixth of the total land area of England and Wales) than in laboratory samples. The use of radiolabeled compounds enabled the workers to follow the path of a given compound or its degradation products through the environment.

Effect of dissolved salts on water solubility of lindane 919

W. L. Masterton and T. P. Lee

Salt effect data for pesticides should be directly applicable to a variety of practical problems. Salts such as the alkali and alkaline earth halides can profoundly influence the solubility of simple organic compounds such as benzene. The effects of 14 different 1:1 salts on the water solubility of lindane have been measured. The greatest decrease in solubility is found with potassium and sodium fluorides; except for the fluorides, the extent of salting out is less for lindane than for benzene.

Energy dispersive X-ray fluorescence analysis of air particulates in Texas 922

J. R. Rhodes, A. H. Pradzynski, C. B. Hunter, J. S. Payne, and J. L. Lindgren

The presence of 17 metals has been detected in particulate matter samples taken from 38 air monitoring stations in Texas. The X-ray technique is useful for air particulate survey measurements and for pollution source location; no sample preparation is necessary, and the method is nondestructive.

Notes

Nerve gas—isopropyl methylphosphonofluoridate (GB)—decomposition and hydrostatic pressure on the ocean floor 928

W. A. Adams

In considering the disposal of toxic materials in ocean environments or in deep-well emplacements, hydrostatic pressure is worth emphasizing since the fate of toxic materials released into the sea or groundwater deep in the earth is dependent on the high pressures found in these environments. For example, the half-life of the hydrolysis of the nerve gas GB increased 25% at a depth of 4000 meters and 69% at a depth of 10,000 meters.

Size distribution of suspended particles from lignite combustion 929

R. E. Lee, Jr. and C. F. Smith

The use of high-volatile content lignite fuel in Ankara, Turkey has been found to lead to the formation of particulate matter with an average particle size predominantly greater than 1 μ in diameter. This size particle is less of an inhalation hazard than the submicron-sized aerosols found in urban air in the U.S. and Britain.

Determination of bis-chloromethyl ether at the ppb level in air samples by high-resolution mass spectroscopy 930

L. Collier

This ether is widely used in the manufacture of anion exchange resins, membranes, and other aromatic products; its vapor is extremely toxic. A procedure has been developed based on mass spectrometry which is useful for detecting the material at the 0.1-ppb level.

Photosulfoxidation of hydrocarbons in the liquid phase 933

P. W. Jones and A. H. Adelman

The fate of air pollutants—sulfur dioxide and hydrocarbons—is the subject of increasing study. This liquid phase study reveals that both hydrocarbon reactivity and the nature of products formed in solution show similarities with aerosol studies under atmospheric conditions.

Credits: 863, UPI; 864, ES&T's Carol Lewicke; 868, ES&T's Stan Miller; 870, Howard Rice; 871, 873, ES&T's Carol Lewicke; 874, Richard L. Renner; 876, 877, U. of Maine at Orono; 880, ES&T's Carol Lewicke; 881, Lubitsh & Bungarz; 882, Joe Phillips; 885, Commercial Testing & Engineering Co.

Cover: Joe Phillips

The International Pollution Engineering Exposition and Congress:

The answers to the problems of pollution control.

The first full-scale effort to deal with all aspects of the massive pollution control problems confronting industry and government will take place December 4-7 in the Cleveland Convention Center: The International Pollution Engineering Exposition and Congress.

If you're an industry executive—plant engineer—government official—consulting engineer—pollution control engineer—this is the all-inclusive event you've been waiting for.

With more than 100 companies exhibiting, it will be the largest industrial exposition yet organized to display pollution control equipment and technology. It will cover the total spectrum of pollution problems, air, water, solid wastes, noise. Projected attendance: 15,000.

The congress, equally broad in coverage, brings national and international experts to discuss the most recent advances in control, here and abroad. A special feature will be experience-exchange meetings for specific industries. With 59 speakers in 36 sessions, the congress will consider pollution on a national and global scale while retaining an emphasis as local as your plant or municipality.

The International Pollution Engineering Exposition and Congress: If you're directly involved in pollution control, you won't want to miss it.

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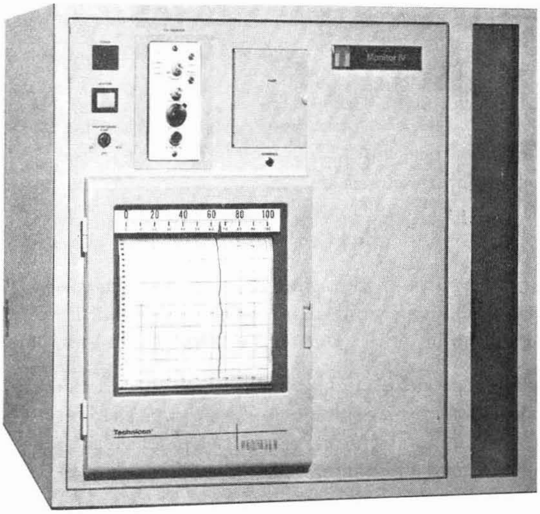

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Stagnation and degradation

DEAR SIR:

What do you mean by "stagnate?" Your August editorial "Can degraded air be clean air?" includes the statement, "Of course, for Miles City, Mont., air that clean (you refer here to air meeting secondary standards) would indeed represent deterioration, but without the option to let its air quality deteriorate a small amount, it is difficult to see how Miles City could do anything but stagnate."

Do you mean that Miles City isn't moving? Of course it isn't—not like New York City or Washington, D.C.—but is anyone really alive in those two cities? People do live in Eastern Montana, and they like it there. Perhaps someday you'll understand that the cry for limits to growth is just the complement of the cry for quality of living—quality which will not be enhanced by increased fouling of the air.

Or perhaps you're already aware that Miles City may soon have its air degraded whether it "progresses" or not. The present plans to denude Eastern Montana with strip mines and to build the world's largest coal-burning power plant directly upwind from Miles City may keep the town from stagnating. The power, of course, will be transmitted to the East where it will be used to air-condition those tombs you call office buildings.

Ron Erickson
Dept. of Chemistry
University of Montana
Missoula, Mont. 59801

Power station water intakes

DEAR SIR:

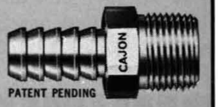
The letter from spokesmen for the British Central Electricity Generating Board, in your August 1972 issue, page 670, was very interesting because it again raised the question as to whether electric utilities, privately or publicly owned, are capable of planning ahead either as to design requirements or market developments.

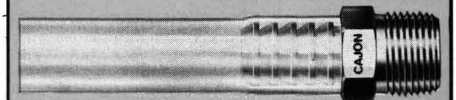
The long-anticipated biological revival of a river such as the Thames would certainly bring with it the small organisms that will, if not treated, grow in cooling systems.

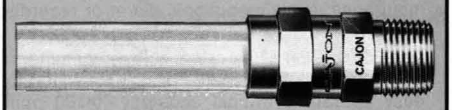
The next question must be asked, I suppose: Were the intake cooling water screens enlarged to deal with larger numbers of larger fish? Or had the newer power plants been "overdesigned," using ancient fish quantity screening needs as a basis? The greater development of lower elements in the food chain ought to lead to more fish, oughtn't they?

Similar questions can be asked about the potential foulers of condensers and the potential pluggers of water-intake, fish-rejecting systems.

Benjamin Linsky
Department of Civil Engineering
West Virginia University
Morgantown, W.Va. 26506







How to tackle the EPA credibility gap

Behind the agency's bureaucratic facade, there are—or should be—technical voices pleading to be heard

If there is one piece of environmental information that consistently impinges on the editorial staff of ES&T, it is that no one seems to know exactly what "the feds" are doing. Or if, by some miracle, someone does know what, he doesn't really know why.

On the face of it, this looks like a sheer case of poor public relations for which the public relations departments of EPA and the other federal agencies should be rapped hard on the bureaucratic knuckles. But there is more to it than that. The fact is, what the government is doing and why it is doing it changes almost weekly, in response to a bewildering array of pressure groups, ranging from militant environmentalists to the Office of Management and Budget. It is sad, but nevertheless true, that EPA has spent much of the two years it has been in existence trying to outguess its many critics and (unsuccessfully) trying to get a jump on what it might be asked to report on/study/analyze/implement next. For instance, our September story on effluent guidelines (page 786) described how the EPA water programs people are currently working up performance standards that will be needed under terms of an act that hasn't even been passed yet (or hadn't at press time). Without this jump, the EPA people feel they couldn't possibly meet the time requirements in the law. Of course, if requirements in that law change drastically, EPA may yet be caught flatfooted.

Part of the blame for this sorry state of affairs can indeed be laid at the door of EPA people themselves. By failing to raise—publicly and understandably—the technical issues that lie behind regulatory (i.e., political) decisions they have unwittingly aided and abetted the perpetrators of the myth that all things are technically possible. And by burying technical expertise under stifling layers of nontechnical bureaucrats and political appointees, EPA's top management has done a disservice to the whole technical community and the country at large.

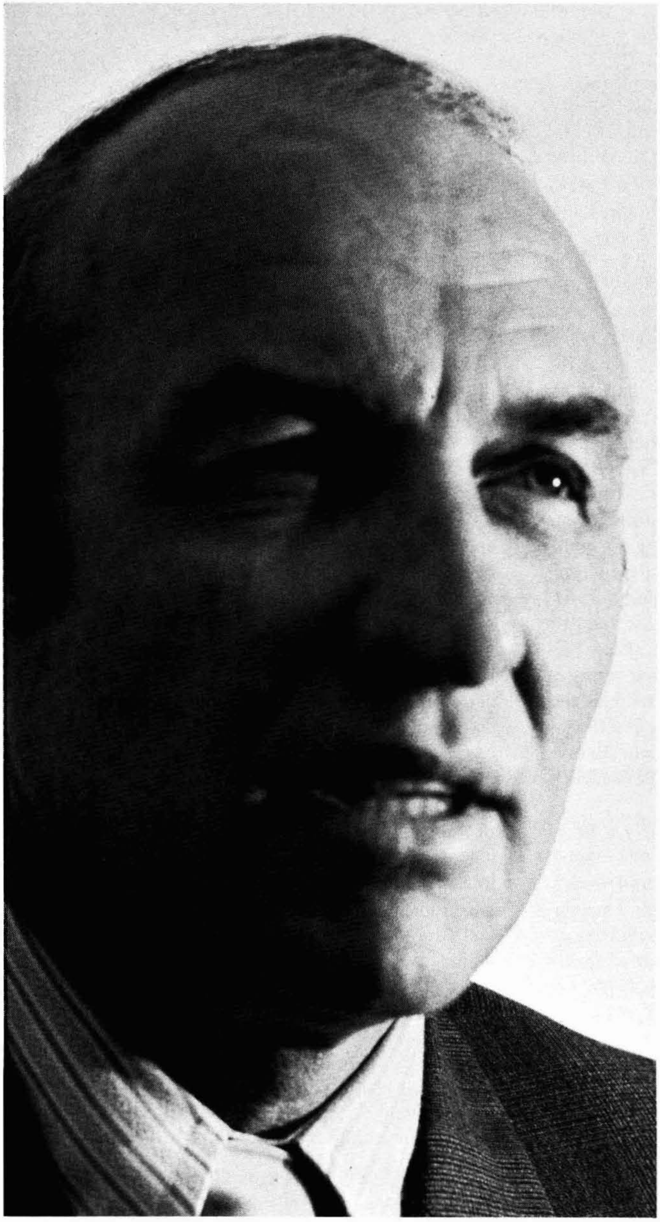
Congress, too, must shoulder some of the blame for a situation in which the executive branch of the government cannot adequately explain to those it regulates the whys and wherefores of its regulations. On the one hand, it has effectively tied EPA's hands, as in the 1970 Clean Air Act amendments where percentage reductions in automotive pollutant emissions were mandated without benefit of a clear technical basis that EPA could use to justify its regulations. On the other, Congress has shown a disturbing penchant for writing into law vague terms such as "best practicable technology" and "zero discharge."

Frankly, we feel that some better means of communication than we now have is urgently needed. The Federal Register may be fine for lawyers, but it is inadequate for almost everyone else. To this end, we are happy to present in this month's ES&T two feature articles (pages 884 and 890) written by technical personnel in EPA. Both are aimed at explaining why the agency did what it did in two instances involving technical expertise and judgment. We think that they deserve reading by all who think the agency acts arbitrarily and by those who genuinely are concerned over the lack of visible justification for federal regulations.

In the final analysis, it will take a major effort both within and without EPA to ensure that everyone understands both what the agency is doing and why it is doing it. ES&T will, of course, continue to try to interpret for readers, as we have in the past, but success may ultimately depend on the skill, perseverance, and sheer guts of technical men and women in government service. We wish them well.

D. H. Michael Bowen

RENT J-M's JACK GARBER.



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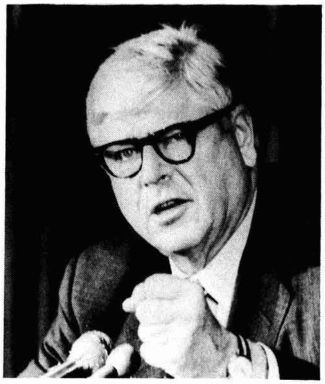
environmental currents

WASHINGTON

Alaska pipeline is a must; oil from shale is coming



Interior Secretary Morton

In a recent statement before the Fairbanks Chamber of Commerce, Secretary of the Interior Rogers Morton said that the Trans-Alaska Pipeline is one of the most environmentally safe undertakings in American history. "The pipeline is critical to our national security," he said. Without it, by 1985 more than half of our oil supply would have to be imported from the politically unstable oil-rich nations of the mideast. Recently, the Interior Dept. and the state of Colorado announced that studies are under way to investigate the environmental affects of oil shale development. The studies are expected to be complete by the spring of 1974 before field oil shale development can begin on a commercial basis.

EPA ups water grants, lets first comprehensive grants

During the month of July, the Environmental Protection Agency awarded grants totaling more than $75 million for constructing or improving waste water treatment facilities, up from $30 million for the same month a year earlier. In June of this year, EPA awarded similar construction and improvement grants totaling more than $210 million. Recently, EPA also awarded its first comprehensive environmental grants to the states of Hawaii, Utah, Washington, and New York. These four grants will support the planning and management of state environmental agencies for fiscal year 1973, and are part of pilot projects designed to test a new EPA grant delivery system where grants under the air, water, and solid waste activities are combined into a single package.

Listen! Small particles are the big pollution concern

Although present technology, if applied universally, can remove more than 90% of all industrial particulate emissions by weight, it cannot remove the small particles which limit visibility and possibly threaten human health. Small particles remain in the atmosphere longer than large ones and are more readily deposited in the lungs. In a recent report from the National Academy of Engineering's Committee on Air Quality Monitoring, it is estimated that the current level of support ($500,000 by EPA) is inadequate to find better controls and should be of the order of $5 million per year over the next 10 years. Chairman of the ad hoc panel on Abatement of Particulate Emissions from Stationary Sources was Sheldon Friedlander of the California Institute of Technology.

Water bill finally emerges from conference committee

In conference since May, the clean water amendments for this year contain a $24 billion authorization for water pollution cleanup, four times more than President Nixon had asked for. Key points include: • funding—of the total authorization, $18 billion goes for municipal treatment plants with the federal share being 75%; • deadlines—best practicable technology for industries by July 1, 1977 and best available technology by July 1, 1983; • goal—zero discharge by 1985. One of the delays involved the matter of hot water discharges from utilities. The conferees agreed that the 1977 and 1983 dates apply to utilities but gave discretionary power to the EPA administrator to waive these requirements on a finding of no harmful effect to water life. The next steps are approval by each House and forwarding to the president for signature.

STATES

North Central power project proposed in Wyoming

The U.S. Bureau of Reclamation is proposing a series of power plants near Gillette, Wyo. that would generate some 50,000 MW of electric power—substantially more electricity than will be produced in the controversial Four Corners complex. The power plants would transmit electricity as far as St. Louis, Mo. Environmental impact studies are under way.

Water reclamation and cleanup under way across the U.S.

Land disposal of wastes

- Michigan State University received the first federal EPA combined construction and research grant last month. The monies (55% federal, 25% state, and 20% local support) will fund a $2.15 million lakes–spray irrigation system for recycling sewage effluent (ES&T, February 1971, p 112). The project, scheduled to be operating by next July, will handle 2 mgd.
- Michigan's legislature has appropriated $25,000 to be used by the state's Water Resources Commission for emergency cleanup of oil and other water pollution spills.
- New York City's Environmental Protection Administration has received signed stipulations from 50 of the city's 200 metal-plating companies agreeing to remove toxic metals from their discharges (ES&T, June 1972, p 518). At least 45 more stipulations are expected shortly. Copper, nickel, zinc, cadmium, and chromium are presently in the discharges.
- Four major river basins are being studied under EPA contract to Water Resources Engineers (Santa Monica, Calif.). Aimed at helping cities, municipal sanitary districts, and state pollution control agencies, the $200,000 computerized studies may make it possible to predict the long-range impact of ecological problems on the basins.

Four river basins under study

Upper Mississippi River Basin
Minneapolis and St. Paul, Minn.
Flint-Chatahoochee Rivers Basin
Atlanta, Ga.
Santee River Basin
Columbia, S.C.
Iowa and Cedar Rivers Basin
Des Moines and Iowa City, Iowa

California cracks down on pre-1965 automobiles

Effective last month, residents of six southern California counties must install an exhaust emission control device on the engines of most gasoline-powered 1955–1965 model cars and light pickup trucks when a change of ownership occurs. About 2.4 million of these vehicles are registered, and about 50,000 are resold each month. The state Department of Motor vehicles will require proof that a device has been installed and is operating properly.

Eight states tackle solid waste management

- Connecticut has contracted General Electric Co. to develop and manage the state's system for disposing of garbage, trash, and other solid wastes with maximum recovery of material and energy. The $1.1 million design phase will be completed by next July with implementation thereafter. The project is funded by the federal EPA, General Electric Co., the Connecticut Dept. of Environmental Protection, Northeast Utilities, and Southern Connecticut Gas Co.
- More than 50 local governments in Alabama, Georgia, Mississippi, North Carolina, Tennessee, and Virginia have received or requested technical assistance from the Tennessee Valley Authority in improving solid waste disposal or establishing countywide rural waste collection systems.
- Cleveland, Ohio has saved $6.3 million or 43% in waste collection systems over a two-year period by requiring householders, rather than collectors, to carry waste to the curb and return the empty cans.

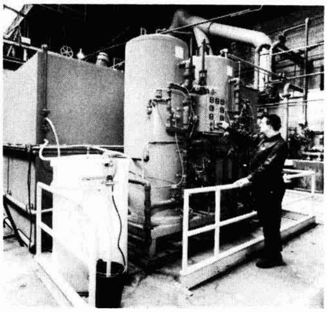
environmental currents

TECHNOLOGY

Device controls small-particle air emissions

The "Pentapure Impinger" of the Purity Corp. (Elk Grove Village, Ill.) is an industrial pollution abatement device which is said to eliminate as much as 99.9% of all particulate matter including submicron particles. Purity president Ladd Pircon says that the impinger is ideal for just about any industry faced with an air pollution problem. The system handles both hot and cold, wet or dry effluents. The unit is in the final patent stages so that the exact process is not revealed. Purity's first installation was made at the Woodruff & Edwards Corp., a gray iron foundry in Tippecanoe, Ind. this May. The unit processed as much as 24,000 cfm eliminating more than 99% of all particulate matter larger than 0.01 μ.

Ion exchange solves chrome waste water problem



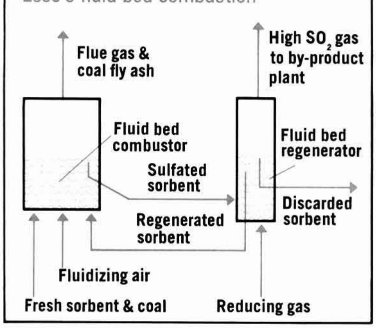
GE's ion exchange system

Ion exchange units designed and constructed by Hytek International (Medina, Ohio) went onstream early this year at General Electric's plant in Cicero, Ill. The unit treats 50,000 gal. of waste water produced each day in GE's chrome-plating operation. The company was faced with significantly reducing the chromate level of this waste because of more exacting restrictions on plant effluents. GE engineer Gene Dillion says, "We took the ion exchange route because it offers a number of major advantages. By utilizing the deionization GE adopted, we completely recondition the water—we condition it to such a degree that we are able to recycle it to our plating system for reuse." He continues, "In this way, we eliminate the pollution problem and at the same time make a big savings in our raw water costs." In this application, Amberlite resins from the Rohm & Haas Co. (Philadelphia, Pa.) were used.

Process avoids need for pollution controls

Magnesium is the major alloying ingredient in aluminum beverage cans. Scrap processed by the secondary aluminum industry averages about 0.5% magnesium, but the Mg content must be reduced to 0.1 in order to make ingot for use in the castings industry. Previous chlorine fluxing procedures were inefficient and created either air or water pollution problems but now Alcoa (The Aluminum Co. of America, Pittsburgh, Pa.) has come up with a fumeless "demagging" process in which magnesium and chlorine are reacted in a closed reactor-settler tank which provides multiple stage gas-liquid contacting, eliminating the need for wet or dry scrubbers and dust collectors. The Alcoa "demagging" system is designed to process 24 million lb of alloy scrap annually at an estimated capital investment of about $75,000.

Pressurized combustion, liquid membranes are being checked



Esso's fluid bed combustion

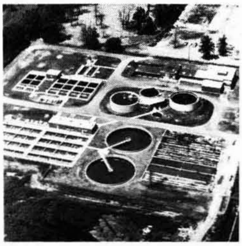
- Engineers at Esso Research and Engineering Co. (Linden, N.J.) are building a pilot plant to test the feasibility of burning high-sulfur coal in a fluidized bed of limestone under pressure. The unit is designed to operate under 10 atm of pressure and a heat release rate of 6 million Btu/hr, equivalent to a 635-kW power plant. The unit is scheduled for completion by mid 1973. Engineers expect the system will be ready for full-scale application by the end of the decade.
- Liquid membrane water treatment technique offers a wide range of potential applications in the area of water treatment, according to other Esso engineers. Subject of recently issued patent, the concept of water treatment with liquid membranes is under bench and small pilot plant studies.

INDUSTRY

Rex Chainbelt has air news and more water news

Rex Chainbelt (Milwaukee, Wisc.), one of the leading water pollution control equipment companies, recently entered the air pollution control equipment field with a gravel bed air filter unit which can be used where very dusty, abrasive, and hot conditions exist such as in cement plants, lime kilns, refractories, and foundries. Rex chairman William Messinger says, "More than 100 major installations in Europe and Asia have proved the effectiveness of the system under a variety of difficulty conditions. There are more than 500 cement plants in the U.S., and more than 80% of them could use this technology." Also recently, Rex Chainbelt signed an agreement with Du Pont to market Du Pont Permasep permeators (reverse osmosis equipment) in Rex-developed waste treatment processes in three areas—to remove dissolved solids from municipal sanitary sewage, hydrocarbon processing wastes, and acid mine drainage.

Chemical plant teams with community on water treatment


Joint treatment on Lake Erie

The B. F. Goodrich Chemical Co., the largest customer of the Avon Lake (Ohio) waste treatment plant on Lake Erie, has joined forces with the municipal operation on a new $3.2 million treatment plant, proof that industry and municipalities can work together on joint regional solutions to water pollution problems. The city began operating its new secondary and upgraded primary treatment plant this April, but Goodrich started up its chemical pretreatment plant last October. The pretreatment plant is an integral part of the entire system, Goodrich's plant manager Robert Rylands says that "this type of effort is going to be needed more and more if industry and government are to make headway in reducing Lake Erie's water pollution control problems."

Steel tries the revenue bond-financing route

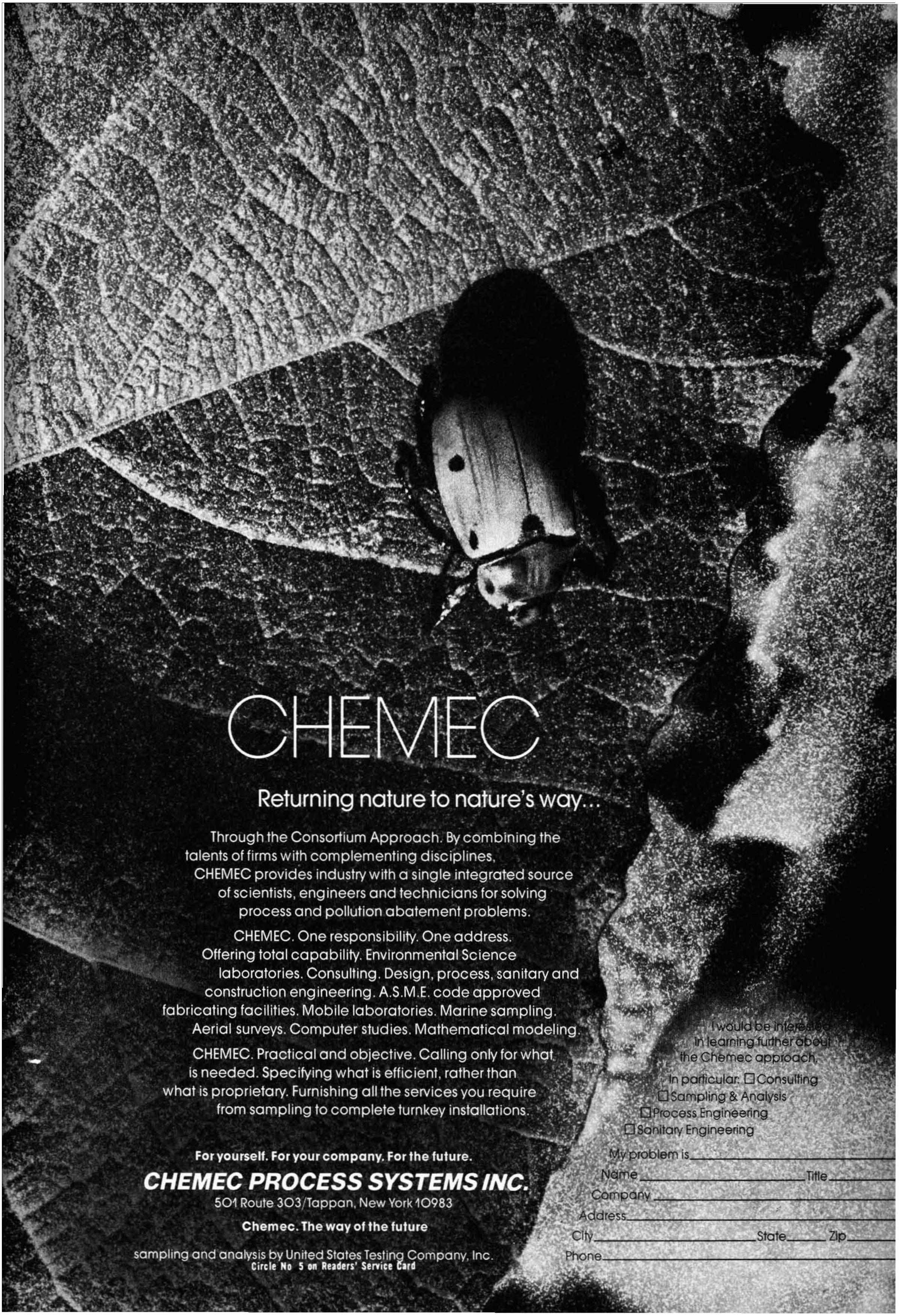
Bethlehem Steel Corp. of Pennsylvania is planning to finance $30 million worth of pollution control facilities at four of its plants in Pennsylvania (see box) in cooperation with the Northampton County Industrial Development Authority. What happens is that the Authority will acquire the facilities through the sales of pollution control revenue bonds and then sell the facilities to Bethlehem. Bethlehem says that this financing method will not add in any way to the burden of Northampton County taxpayers, but would help expedite the company's comprehensive program of environmental quality control for which it has already spent more than $200 million.

Controls for Bethlehem's Pa. plants

BETHLEHEM PLANT	
Air quality control, new coke battery	$5.6 million
Desulfurization, all-coke oven gas	$5.4 million
Air and water, specialty facilities	$1.5 million
STEELTON PLANT	
Electric furnace fume collection	$6.0 million
LEBANON PLANT	
Collection and recirculation of mill waste waters	$2.6 million
JOHNSTOWN PLANT	
Desulfurization, coke oven gas	$5.5 million
Blast furnace fume collection	$2.6 million
Pig machine for fume collection	$0.3 million

All American shredding plant opens in Delaware

All American Environmental Control Corp. (Wilmington, Del.) started up its 1200 ton/day shredding plant for New Castle County. The plant handles 70% of all the refuse collected in the county and reduces its volume, making it easier to compact and extending the useful life of the county's landfill. In operation, a magnetic belt downstream of two hammer mill lines removes steel cans (estimated at about 500 million per year) which will be sold to M. & T. Chemicals Inc. (Baltimore, Md.) for detining and subsequent remelting into new steel. All American also favors the idea of composting the shredded biodegradable waste and using it directly in the nearby Pennsylvania mushroom industry. The planned Hercules 500-ton/day plant (ES&T, September 1970, p 729) is stymied due to lack of federal funds.



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ES&T interview

Thomas O'Boyle

Thomas O'Boyle is president of Ecodyne Corp., a subsidiary of Trans Union Corp. Incorporated in 1970, Ecodyne is running hard to be the No. 1 water company in the U.S. O'Boyle tells ES&T's Stan Miller that Ecodyne is the largest diversified company devoted exclusively to water treatment, water cooling, and waste treatment. The company does about everything one can do to water—cools it, cleans it, softens it, conserves it, treats it, recycles it, uses it, and protects it. Ecodyne sales hit $75 million last year (calendar year), out of $255 million for Trans Union, up from $65 million and $200 million, respectively, in 1970.

Rationale

Is Ecodyne ready for passage of a new water pollution control bill?

That question should really be answered in two parts. Do we have the technology to handle the demands which will arise under the new water bill? And, do we have the manpower and physical capacity? Frankly, there is no question but that from a technology standpoint Ecodyne can easily handle any demands for advanced waste water treatment. As I have said many times before, the processes and techniques for effective control of water pollution have been available for years and our expertise in this field has solid depth. From a manpower and capacity standpoint, in many of our divisions we have already anticipated a growing market potential and have geared up our operations to cope with it.

When you say "geared up," how much expansion do you anticipate?

We could probably double the municipal waste water treatment output of our Smith & Loveless Division without any problem whatsoever. We can handle our share of biologically treated industrial waste. Our Graver Division which handles both physical-chemical municipal waste treatment and chemical treatment of large industrial wastes, is an engineering company subcontracting to independent fabricators. There is no reason why we cannot substantially expand Graver's output since we have no plant restraints. Frankly, the only problem we would have at Graver is the ability to recruit competent engineering personnel to handle increased volume. This is always a problem in a high-technology, custom engineering company. We have learned to live with this problem over the years. As a matter of fact, engineering talent seems to be more available today than it was a few years ago, so I see no problems here.

On the cooling side, we have grown considerably over the past few years and have already expanded our facilities severalfold. I might note that because of the long lead time required on major cooling tower jobs, our cooling group can book considerably more business and still have ample time to add to its physical staff and capacity on a planned schedule.

Where should the national focus in water pollution cleanup be at this time?

It's not glamorous but it's absolutely essential that we, as a nation, upgrade a vast number of municipal treatment plants that are currently operating with inadequate primary and secondary treatment facilities. In industry's case, there must be a real attempt to formulate consistent standards throughout the U.S. so that an industry in one state does not have a competitive advantage over a similar industry in another state. It's better, in the long run, to pursue a methodical solution to the municipal and industrial problems. The recent actions against phosphate detergents and DDT are examples of crash programs instituted by emotional issues rather than logical ones.

To what extent is there a delay in the nation's water cleanup activity?

Well, it is rather difficult to quantify. As a nation we have lost a couple of years because of a lot of talk and little action. On the funding side, the federal government has consistently under-obligated appropriated funds. We can catch up, but it is becoming more expensive to do so. Still, we have the ability to catch up, and I am sure we will once meaningful federal legislation is enacted.

Position

If Ecodyne is the No. 1 water company, what company is No. 2?

Thanks for your vote of confidence. Seriously, we have taken the position that we are the largest diversified company exclusively in the water field. Our broad product line and our substantial sales volume, again exclusively in water, certainly supports our claim. When you ask what company is No. 2, what you are asking is "who is our main competitor across the board?" Unfortunately, there is no simple answer to that question. The fact is there is no single competitor that we meet head to head in every line of our business. There is no single company that does all the things—water treatment, water cooling, and waste water treatment that Ecodyne does. Certainly, there are companies that are larger in specialized segments of our market but the real point is that Ecodyne has achieved a commanding position in the most important areas of the water field.

Does Ecodyne anticipate any move into other pollution control areas?

At the moment, no. We feel strongly that our future in water is so challenging that water can absorb all of our energy over the next few years. If a particular and unusual opportunity presents itself, then we might reconsider, but at the moment we have no plan to go into other areas. The Ecodyne philosophy is to establish a dominant leadership position within a given industry. It would be inconsistent with this philosophy to go into another industry such as air, for example, unless there was the potential to achieve a commanding role. There doesn't seem to be any opportunities like this at the present time.

I understand that Ecodyne is only two years old. Don't your roots go back farther than that?

We've been in the water field since we acquired Graver in 1957 and Graver's roots go back to the 1940's. In our later acquisitions, we've stayed in the water field, and the water field alone. So, over the years, we've built our reputation in water. We acquired Lindsay and Smith & Loveless in 1959, and formed Unitech in 1967. In 1968 all of these divisions, each of which was operating successfully, were brought together into the water and waste treatment group of Union Tank Car Co. which subsequently became Trans Union Corp. So Ecodyne was operating as a single company, in a sense, as the water and waste treatment group of Trans Union in 1968 with the history of its division going back some decades. In 1969, we purchased Fluor Cooling Products, now Ecodyne Cooling Products Co., a company which dates back to the early 1920's. This was our entry into the evaporative cooling tower business. And in 1971, we acquired McKenzie-Ris which is in the air-cooling field.

Products and services

What is the breakdown for Ecodyne's sales?

Ecodyne's total sales in 1971 were divided among the following four markets: Industrial, $33 million; Electric utility, $17 million; Municipal, $14 million; and Residential, $11 million.

What percentage of the sales is equipment; what percentage is engineering services?

It's all equipment sales. The engineering Ecodyne does is always in connection with the sales of its products. We do not charge separately for engineering. We may have a specialized charge for field services, repair work, that sort of thing, but we have no separate charge for basic engineering. The engineering costs associated with a particular installation are included in the overall price of the product along with other material and labor costs.

Does Ecodyne retain the services of consulting engineering groups? Does the work that you do come in the door by the consulting engineer, from the municipality, or does Ecodyne have a marketing group that helps?

Let's break those questions down. On the municipal side, consulting engineers are practically always involved. The work comes to us through our sales offices or representatives who keep in touch with potential clients and consulting engineers to discover what jobs are coming up. On the other hand, industrial customers often utilize their own engineering staffs to perform studies and make recommendations on treatment needs.

The one exception seems to be in the utility field where large consultants are often used. Depending on the size of these consultants' staffs, industrial customers may never deal with a consulting engineering firm. In this case, our field sales force deals directly with the industrial customer involved. Many inquiries come directly to us because Ecodyne is well-known in its fields. But there is always a lot of bird-dogging that goes on to see that sales offices and representatives do not miss an opportunity.

Turn-key

What is the present company position on turn-key construction, both municipal and industrial?

We have no inflexible position on it. We are capable of doing turn-key jobs although we have not done any great number of them up to the present time. In the municipal field we have done none, but in the industrial field, we have been involved in several turn-key projects. As a matter of fact we have recently bid on a number of such projects in Canada. There has been a lot of comment lately that more and more industrial companies are turning to turn-key projects. It is true that there has been more interest in this type of approach on industry's part, but

Ecodyne milestones in water and waste water treatment

1972: Contract awarded for first U.S. physical-chemical municipal sewage treatment plant to Graver

1971: Introduction of the concrete mechanical draft cooling tower

1969: Tertiary filters for reducing municipal sewage effluent to potable water quality levels following secondary activated sludge treatment installed by Smith & Loveless

1969: First "'PFR' concentrator producing 63% solids black liquor from southern pine for direct firing into odor-free recovery boiler designed and furnished by The Unitech Co.

1966: Introduction of PVC fill in cooling towers to replace wood by Ecodyne Cooling Products

1962: Powdex$^{(R)}$—High-quality condensate polishing for electric utilities

1956: First use of sewage plant effluent for boiler feedwater after treatment by Graver clarification, filtration, and ion exchange

1946: Factory-built sewage pumping stations pioneered by Smith & Loveless

1946: Phosphates reduced to negligible level by first Graver tertiary treatment plant designed to recover industrial process water from sewage effluent to supply cooling water for oil company

1921: First cooling tower for an oil refinery built by Ecodyne cooling products predecessor

"We feel strongly that our future in water is so challenging that water can absorb all of our energy over the next few years."

Ecodyne's O'Boyle

I really can't say that we've seen any evidence of a trend. In the municipal field we just don't think the votes are in yet. I can't really say whether municipalities will move in this direction or not, but I doubt it. Ecodyne can handle any turn-key opportunities which might arise. If the market demands turnkey, Ecodyne can be counted on to provide it.

What are the problems of industrial users of municipal waste treatment plants?

There may be a very severe economic problem for industrial users with a surcharge program. Once the industry is liable for surcharge there seems to be a very automatic way that the additional costs are passed along to industry rather than absorbed by the municipality. Surcharges, of course, are not applicable in all waste water treatment agencies. The Metropolitan Sanitary District in Chicago has a surcharge program. Some other municipalities do also but, at the moment, only a minority of agencies have surcharges. You would expect to see more and more programs like these because one of the provisions of the new water bill requires that the industrial user pay his prorated share of the treatment cost of the municipal plant. Of course, industry can always make other arrangements to handle its waste. By bringing wastes down to the acceptable municipal standard, industry can eliminate not all, but probably most, of a surcharge.

Marketing

How does Ecodyne resolve in-house squabbles between competing technologies, such as physical-chemical treatment vs. biological treatment of municipal wastes?

Fortunately, to date, any squabbles we might have within the company are theoretical rather than commercial. Naturally we have strong advocates of both biological and physical-chemical systems within our divisions. I think this is healthy. There is nothing like a vigorous competition of ideas to promote the development of the art.

On the practical side, almost invariably the process that is going to be used in a particular application has already been decided on by the customer and his consulting engineer when the job comes to Ecodyne. In other words, it has already been specified whether a biological or physical-chemical process will be used. The same is true in the cooling field. The customer has decided that he needs an evaporative cooling tower or an air-cooled heat exchanger by the time he comes to Ecodyne. Up to now the marketplace has not generated any real squabble between competing technologies. As an aside, it gives me some reassurance that whatever the technology chosen, Ecodyne can provide it.

Is there a marketing function in Ecodyne which resolves differences? Who figures the best economical and financial fix for the use of any particular technology?

We don't have a corporate staff marketing function, if that's what you mean. We haven't adopted that kind of an organization structure. Ecodyne is organized to stress the autonomy of the divisions, but it is also flexible enough to handle a joint approach to a specific problem. There is constant communication between all levels of our divisions: marketing, research and development, and product planning. This relationship is not as difficult to foster as you might think. We also have regular meetings of the division presidents to examine product strategies, research and development activities, and to concentrate our marketing efforts more effectively. Solid decisions come out of these meetings. Positions are set and product and process responsibilities are allocated. No, we don't have any trouble resolving differences. It works very well.

Technological innovations

It has been said that all of the technology is available today to solve all the problems? If Ecodyne is innovative, then must the innovations of necessity be more economical?

Not necessarily. The basic technology is available today but we need continuing innovations and refinements, not only to improve the effectiveness of that basic technology, but also to broaden its applications. For example, the principle of the cooling tower is the same as it was 50 years ago. Ecodyne has made substantial strides in improving the efficiency and design of these towers but not all of these improvements have reduced the cost of the towers: for instance, the PVC fill material which replaces wood. The PVC fill is not less costly, but other advantages, such as fire resistance and improved thermal performance, accrue from its use. So, innovations do not necessarily have to be more economical.

In the physical-chemical area, the Rosemount, Minn., job is a refinement of technology that has been available for years. We are just designing it into a highly efficient system. The same is true of biological treatment plants where we are continuing to up-grade, refine, and shorten the treatment cycle. So not all innovations reduce the cost; they improve the product. Basically, we are still using a time-tested technology. There are no black boxes that have appeared and there are not likely to be any.

What are the major innovations introduced by Ecodyne for better water and waste treatment?

Ecodyne has a history in the water treatment field running back to the 1920's. We introduced significant innovations even in those days. As you can see (box, p 869), we have continued to innovate up to the present date.

outlook

Recycling sludge and sewage effluent by land disposal

Spray irrigation purifies discharges and wastes from treatment plants while it enriches soil and recharges groundwater

Over 23 billion gallons of sewage effluent are discharged daily by municipal treatment plants. These treated waste waters, even if acceptable to federal and state water quality standards, are usually enriched with dissolved minerals and residues which may speed up eutrophication and deplete the dissolved oxygen in the water necessary for aquatic life. The same waste water treatment plants are confronted yearly with millions of tons of sludge accumulated from waste water treatment. Also, increasing demands for municipal water supply can and are causing serious water shortages by utilizing groundwater but not replenishing it.

One possible solution is land disposal of treated sewage and sludge. Land disposal itself is not new. It has been practiced for years, though mainly in industrial applications. For example, Seabrook Farms (Seabrook, N.J.) sprays cannery and food processing waste water on its crop and forest lands. Land disposal is also practiced in other countries. Germany, Holland, India, England, Australia, Canada, Turkey, Greece, Puerto Rico, Czechoslovakia, and others are using or experimenting with land disposal. However, land disposal of sewage and sludge effluents is a more recent innovation.

What is land disposal? It is generally characterized by spray irrigation or application of sewage effluent or sludge slurry on forest or cropland in predetermined rates and amounts. Land disposal is based on the "living filter" concept—letting nature recycle nutrients and water beneficially on land rather than detrimentally through streams and lakes.

Actions and reactions

In spite of its good points, land disposal cannot be undertaken capriciously. Pros and cons were pointed out at the Symposium on Recycling Treated Municipal Waste Water and Sludge through Forest and Cropland, sponsored by Pennsylvania State University and others, at University Park, Pa., in August.

Sewage effluents and sludge from waste water treatment plants reflect the quality of the original waste water and modification by the particular treatment process. Therefore, effluents vary in volume, strength, and composition as well as being dilute, physically inhomogeneous mixtures.

As with sewage effluent, the chemical character of sludge is reflected in the sewage source and method of treatment. To safeguard health, only heat-dried, air-dried and stored, or digested sludge should be used on cropland, says J. R. Peterson, Metropolitan Sanitary District of Greater Chicago Research and Development Laboratory. No known case of human or animal disease has been reported with these forms of sludge.

Wildlife. *Researchers keep close tabs on animals living in irrigated areas*

The long-term capability of the soil to act as a physical filter is closely related to chemical and biological interactions after treated sewage effluent is applied to the soil. The key to maximum use of the soil filter is water management and movement. Clogging or standing water will deter the filter and cause runoff. The area will then become anaerobic with accompanying odor, gas production, and unsanitary conditions. Clogging can be controlled by cyclic applications of sewage up to soil capacity (a sandy soil can transmit effluent more rapidly than a fine clay soil).

Chemical functions of the living filter during irrigation include ion exchange, adsorption and precipitation, and chemical alteration. Soils are known to absorb 1000–3000 lb/acre of phosphorus to a depth of 3 ft. However, if overloaded, the soil will cease to remove phosphorus. Some sulfate, boron, and heavy metals are also removed from waste water and sludge by adsorption. The capability of soil to handle nitrogen is the limiting factor for land disposal of sludge, explains T. D. Hinesly, University of Illinois (Urbana, Ill.). Phosphorus is the second limiting factor.

In general, precipitation reactions, depending on pH, occur after adsorption reaches completion. The soil not only chemically filters but also may chemically alter components of waste water it contacts.

As a biological filter, soil contains microbes, animals, and higher plants. Bacteria numbers run into the billions, but that number decreases rapidly with depth.

Soil microbes decompose and metabolize biodegradable organic materials to carbon dioxide and water. The decomposition rate depends upon the soil; the majority of sludge decomposition occurs within the first month. Microbes also degrade or detoxify potentially toxic or unwanted organic compounds, for example, pesticides, phenols, or NTA. Phenols will decompose as long as there is sufficient residence time with microorganisms, explains Robert H. Miller, Ohio State University (Columbus, Ohio). Microorganisms modify adsorption and mobility of cations and anions (including phosphorus and heavy metals) within the soil profile, modify the adsorption of nutrient elements and heavy metals by plants, and transform nitrogen.

Pathogenic organisms die rapidly in a soil environment. Few disease incidents are related to land disposal, explains D. H. Foster, University of Illinois (Urbana, Ill.), but caution should be exercised in treatment and handling effluent and sludge.

Choosing a site

A number of hydrogeologic factors must be considered when selecting sites for land disposal of sewage and sludge. Each site has its own characteristics, and soils, topography, climate, geology, hydrology, and vegetation must be taken into account. But these aren't the only factors, stresses Richard R. Palizek, Penn State University (University Park, Pa.). Other important considerations include:

- nature of the waste water to be treated
- season of the year water is to be applied
- slope, thickness, and physical-chemical characteristics of soil and rock including infiltration and drainage
- local and regional hydrogeological setting
- water quality standards to be met
- design and operation of a monitoring network
- administration and regulatory requirements
- collection and reuse systems
- dewatering requirements.

This large number of considerations is necessary to avoid salinity buildup, drainage difficulties, putting water in a discharge area rather than a recharge area, lateral movement of water if there is a hardpan, plow sole (compacted layer of earth caused by repeated plowing at the same depth), or caliche (a crust of calcium carbonate) in the soils, freezing in winter, and maintenance problems. After variables are chosen or dealt with, there is no problem with engineering design, emphasizes Earl A. Myers, Penn State University.

What are the effects of this irrigation on plant and animal life? Researchers around the country find that the height and diameter of trees are greatly increased for better pulpwood. Crop yields are larger. Growth of both forests and field crops is lush and exceeds similar areas without irrigation, explains William E. Sopper, Penn State University.

Penn State scientists have deer and rabbit populations in treated areas. Because of increased forage quality, all species readily feed in irrigated areas and have no apparent side effects. In fact, these animals are often in better health than animals with less nutritious forage.

Experiments and applications

If all municipal waste waters in the continental U.S. were given secondary treatment and the resulting solids stabilized, about 10–12 million dry tons of solids would be available each year. If these solids were applied to meet the needs of nonleguminous crops for supplemental nitrogen, it would require about 10 tons/acre. Thus, over one million acres of land would be needed to utilize all sludge solids. There are 465 million acres of cropland in the U.S.; 0.5 million acres of strip-mined land exists now, and another 0.5 million acres will be strip-mined in the next 20 years.

Penn State has experimented with spray irrigation of sewage effluent since 1962 on about 65 acres of forest and cropland. Thus far, the "living filter" project has efficiently removed 99% of the phosphorus from the percolating effluent. Effluent nitrogen concentrations were reduced 61–85% in land disposal. Both crop yields and forest growth increased. Changes in soil chemistry—for example, exchangeable calcium, potassium, etc.—are small and do not appear to be a future problem, comments Louis T. Kardos, Penn State University.

In Arizona, the feasibility of renovating secondary sewage effluent by groundwater recharge is being considered for the Salt River bed near Phoenix, Ariz., where the water table is dropping about 10 ft/year.

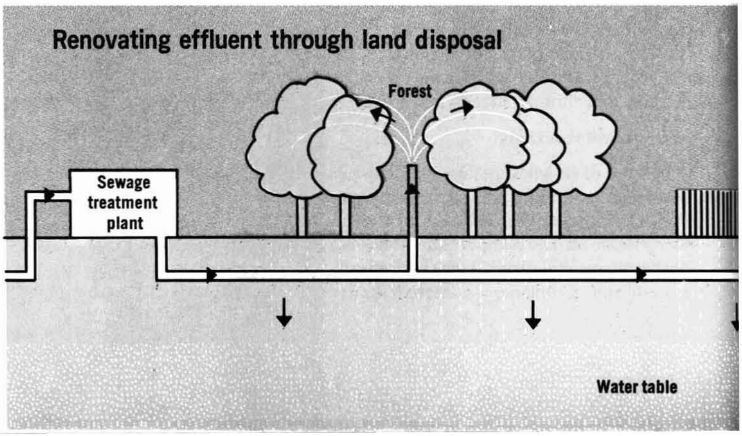
The Salt River bed is usually dry and an excellent area for groundwater recharge. Secondary effluent would be recharged into the ground through basins and later drawn up through the river bed for irrigation and recreation. The price tag for putting effluent underground and pumping up water for use is estimated at $5/acre-ft (tertiary treatment costs would be 10 times as much.)

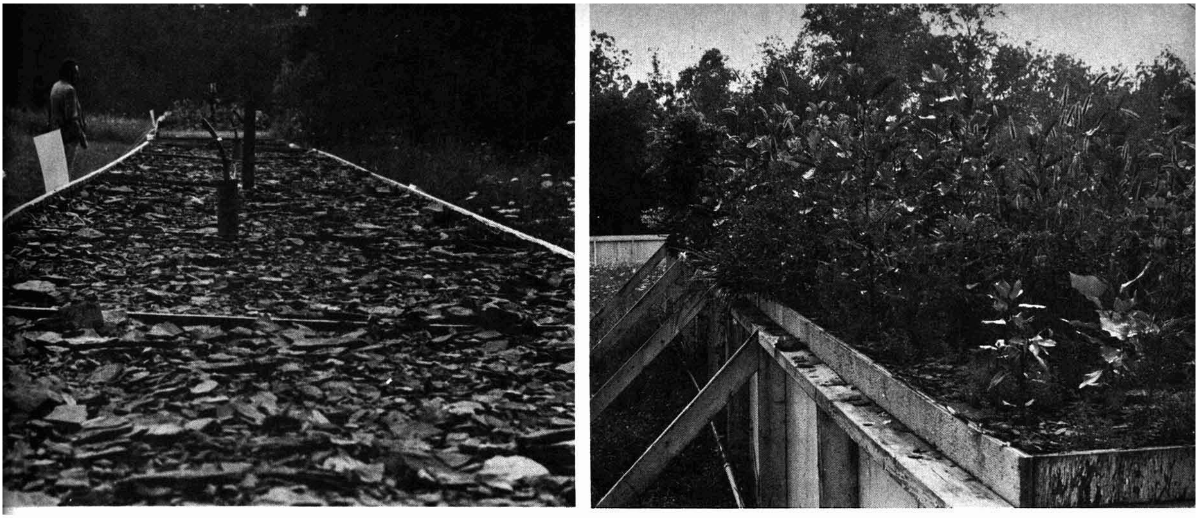
Six experimental basins were constructed for initial testing and filled with secondary sewage effluent. Water sampled from test wells showed that suspended solids, BOD, and fecal coliform were completely removed as the water seeped through the soil.

One widely publicized waste water treatment system is the Muskegon County, Mich., irrigation system. This project is designed to irrigate now barren farmland with waste water from the sewers of 13 Muskegon County towns and five industrial plants which now empty into Muskegon and Mona Lakes. The $36 million system is presently under construction, and a $2 million pilot operation will begin in 1973. The complete project will utilize 43–90 mgd within 10 years.

Reclamation

A use for sewage sludge is restoring strip-mined areas. Researchers from the U.S. Forest Service applied treated anaerobic sludge to acid-producing land previously stripped for coal in the Shawnee National Forest in Southern Illinois. The runoff from this stripped land contained 4000 mg/l. iron, 2000 mg/l. aluminum, pH 2.3, and acidic concentrations of 24,000 mg/l. After applying the sludge, water quality changes included 60% or greater reduction in acidity, iron, aluminum, and manganese concentrations. And





Effects. *Strip mining slag does not normally support vegetative growth (left); however, when irrigated with secondary—treated sewage effluent, the lush growth and resulting ground cover (right) can reclaim useless land*

the area supported nearly 100% vegetative cover. The Forest Service is now planning to use sludge on 77 hectares (one hectare equals 2.47 acres) of stripped land.

Chicago plans to handle some of its wastes with the "Prairie Plan." Over 10,000 strip-mined acres have been acquired in Fulton County, Ill. (200 miles away by river) to handle solids from the Metropolitan Sanitary District. The operation began last year when 630 acres were graded and 500 acres were irrigated and planted with crops. By the end of this year, contracts will be completed to enable solids to be recycled from a two million population. The cost of the Prairie Plan is now $50/ton; however, $34 of this is for transporting sludge by water. When a pipeline is built, expenses will be reduced.

University of California and U.S. Forest Service researchers are spraying sewage effluent in the chaparral and sagebrush lands in the western states. The population in the mountain communities has increased so rapidly that waste treatment facilities are not adequate. Also, there are numerous brush fires in this dry area. Land disposal may alleviate both problems by providing effluent treatment and maintaining "greenbelts."

The town of Falmouth, Mass. (located on Cape Cod) is in final stages of design for land disposal of its wastes instead of ocean disposal. In face of ocean dumping bans, Philadelphia is canvassing bids for land disposal of its sludge. A combination lake-spray irrigation system designed by the Institute of Water Research, Michigan State University, will be in operation next summer in East Lansing, Mich. (ES&T, February 1971, p 112).

On a smaller scale, in Mt. Sunapee State Park, N.H., septic tank effluent is stored and stabilized in oxidation ponds and then sprayed over a somewhat hilly forest area. Williams and Works (Grand Rapids, Mich.) has designed 16 pond and irrigation systems to serve 63 to 9000 people.

Governmental viewpoint

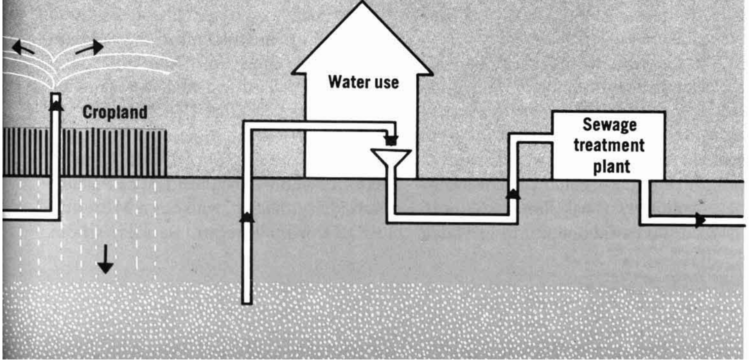
State and federal agencies are taking a hard look at land disposal. Guidelines for ground disposal of waste waters were adopted in 1971 by the Great Lakes–Upper Mississippi Board of State Sanitary Engineers. The state of Michigan has utilized these guidelines as framework for planning, designing, and managing some 50 municipal projects.

In August, the Pennsylvania Department of Environmental Resources published a guide (not regulations) for environmentally safe land disposal operations. Officials purposely avoided publishing required criteria to be met since each site is different. There are 75 operating spray irrigation systems in Pennsylvania, and 10–20 more are applying for operating permits.

The Corps of Engineers is studying land disposal for the Chicago metropolitan area and other parts of the country. At least 26 sites on national forest land are in various stages of projects for sewage and sludge disposal. However, sewage containing chemicals forbidden by U.S. government for use in agriculture cannot be sprayed on government lands. The U.S. Forest Service has set up criteria for effluent spraying on government lands.

The federal EPA has awarded grants for land disposal studies, and is encouraging the practice with the necessary precautions. Federal guidelines have not yet been published.

Officials and scientists alike emphasize that land disposal of municipal sewage and sludge is just one technique, not a panacea. As an alternative for other advanced waste treatment systems, land disposal shows a great deal of promise. CKL



Putting industrial sludges in place

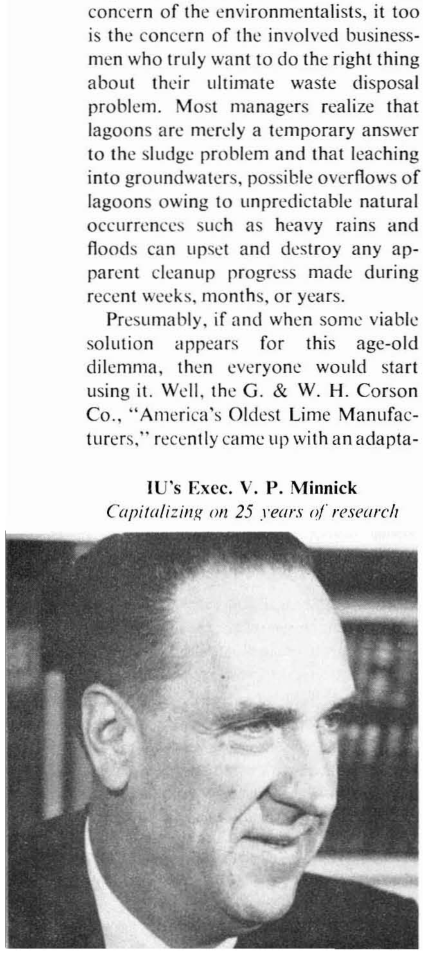
No longer must industry wonder what to do with by-product sludges, for now these waste materials are being encapsulated by IU/Conversion Systems, Inc.

Take a mixture of fly ash and industrial by-product sludge, add a dash of hydrated lime, cure at ambient temperature, all according to a patented process, and your industrial sludge problems are over. Does it sound too simple? Will it work? It's not really as simple as a mere mention of the ingredients, but work it will. The resulting material is a nonleachable, sanitary structural material that may be the innovative answer to the sludge disposal problem.

What to do with sludges, the manmade by-product of 20th century technology, has plagued managers of industrial operations since the 20th century began. Sludge disposal is not only the concern of the environmentalists, it too is the concern of the involved businessmen who truly want to do the right thing about their ultimate waste disposal problem. Most managers realize that lagoons are merely a temporary answer to the sludge problem and that leaching into groundwaters, possible overflows of lagoons owing to unpredictable natural occurrences such as heavy rains and floods can upset and destroy any apparent cleanup progress made during recent weeks, months, or years.

Presumably, if and when some viable solution appears for this age-old dilemma, then everyone would start using it. Well, the G. & W. H. Corson Co., "America's Oldest Lime Manufacturers," recently came up with an adaptation of its previously developed process that promises to solve the problem by encapsulating the sludge into a structural material which can be put in place once and for all. Not only does the solution take care of the sludge disposal problem but it puts the encapsulated waste material to good use as roadbed material or construction material that is sanitary and nonleachable, or construction aggregate which meets ASTM standards.

IU's Exec. V. P. Minnick
Capitalizing on 25 years of research

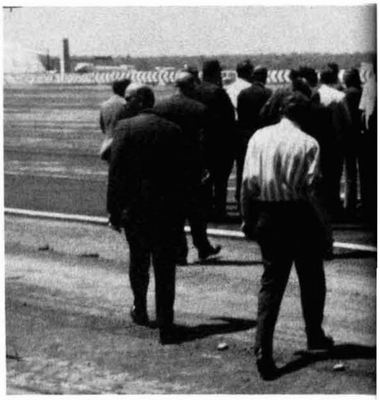


All outward appearances indicate that Corson Co.'s answer to the sludge problem is certainly going places, at least considering the facts that:

- the 150-year-old company, operating since 1822 in the Whitemarsh Valley in suburban Philadelphia, was acquired by International Utilities Corp. (IU) on March 22, 1972
- IU, with annual sales of $1.2 billion, is a company diversified in land transportation, ocean shipping, utilities, industrial products and services, land development, and agriculture
- IU/Conversion Systems, Inc. plans to capitalize on its recent acquisition's encapsulation technology, which IU calls the Poz-O-Tec process
- there have been several successful field demonstrations of the Poz-O-Tec technology to date, and proposals for further work are being prepared.

Now IU has determined to bring the efforts of the research-oriented Corson management to market. One factor that made the Corson acquisition so attractive to IU was that Corson is one of the very few lime companies (of the approximately 140 lime operations in the U.S.) that has had a laboratory largely directed to basic research, some 25 members strong.

Over the years, the Corson management recognized the value of innovation and research, which have moved them out front. Corson's reputation for technical excellence is acknowledged by the entire lime and pozzolan cement industries. Similarly, IU has shown ability to carry on successful operations in a wide range of different business areas, and it has high hopes that it will have similar success in bringing the Poz-O-Tec process to market.



What's behind the development?

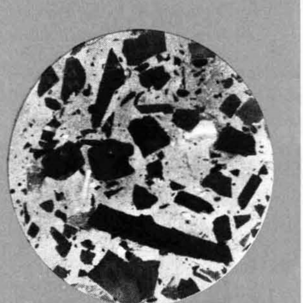
One of the major contributions from Corson's research has been the utilization of pulverized coal fly ash. Since 40 million tons of this by-product material, produced by utilities burning pulverized coal in their production of electricity, are produced annually—and estimated to increase to 50 million tons annually by 1980—there is little hesitancy to label the Poz-O-Tec encapsulation development as a breakthrough. Especially because lime scrubbing of stack gases of electric utilities for SO_2 removal is an upcoming technique for SO_2 removal, the potential applications of the new technology appear endless.

The man behind the development of the Poz-O-Tec process is L. John Minnick, presently vice-president of research and development of the G. & W. H. Corson Co. Before the name of IU's new subsidiary had yet been finalized, IU had revealed that Minnick will be the venture's executive vice-president.

IU has teamed Minnick with Leon V. Hirsch, who will be president of the new subsidiary. Hirsch, who has a MBA and a DBA from Harvard Business school has had experience in the starting of business ventures from the ground up, both at Xerox Corp. and the Franklin Mint Corp.

When Minnick joined Corson in 1937 he was presented with the challenging assignment of developing "improved products." Over the years, some 30 patents have resulted from his research, with the culmination being the encapsulation technology for incorporating fly ash, lime, sulfate, and water into a rigid solid material. One of the keys to encapsulation of this four-component system is the presence of sulfate, which is very important for the ambient temperature cure reaction to occur. More than five years ago, Minnick recognized this fact.

Some of the patents, for example, include a basic claim on the incorporation of fly ash into a composite material which is the well-known Poz-O-Pac. The Poz-O-Pac material is basically a stabilized road base that costs about $3.50/ton and is composed of a small amount of lime mixed with a larger amount of fly ash, with the bulk of the material being aggregate. Other patents include one for dispersion of dry lime in the fly ash, a second for the addition of sulfate to enhance the Poz-O-Pac reaction for ambient cure reaction, and a third for the incorporation of mine tailings into the Poz-O-Pac mixture.



Field demonstrations. *Sludge material was used for a 120-acre road bed surface at Transpo 72, Dulles International Airport; cross section is shown of General Battery Corp.'s sludge using battery casings as aggregate*

Research in this area has been fruitful, and the patents that have been issued attest to this. For example, one development should prove useful to the new IU venture as certain SO_2 removal technologies take hold (ES&T, August 1972, p 688). Another example relates to a composition of fly ash containing lime and sulfate that should prove useful and effective as the dry lime (or limestone) injection processes take hold. A further development relates to a calcium sulfite base sludge which should prove useful to the new IU subsidiary as the wet scrubbing technology is applied throughout the electric utilities industry.

Of course, this recognition opened up an entirely new process with great potential because the fly ash—the waste material from the electric power generating industry—along with the lime which the utilities can use for SO_2 removal techniques can be combined so that the worrisome by-products from the generation of "clean power" can be put in place once and forever.

The IU subsidiary plans to go into the chemical industry and get rid of that industry's burdensome by-product sludges, or at least the inorganic ones. Sludges resulting from the neutralization of acidic mine water with lime can also be encapsulated. A number of patents have been issued or applications are pending on "an improved product" which basically reflects the fruits of a 25-year research effort. The number of applications seems boundless.

Getting the business

How soon all utilities rid themselves of a commonly shared disposal problem is something the IU venture would keenly like to know; it is out for the business. The IU subsidiary has the firsthand know-how for encapsulating the various sludges, and it hopes to get the business of sludge producers including:

- sludges from electric power generating plants resulting from wet scrubbing of stack gases with lime for SO_2 removal. These plants also are involved with the fly ash disposal problem
- sludges resulting from the treatment of acid mine drainage waste waters with lime
- sludges, at least the inorganic ones which are by-products from the chemical industry. (The presence of organic materials, in some instances, disrupts the ambient cure encapsulation reaction.)

To date, this encapsulation technology has been used in several field projects. In one application, the material—essentially fly ash, lime, sulfate, and water—was used for a 120-acre road bed surface at TRANSPO 72, Dulles International Airport (Virginia), and in another application, a sludge containing lead and shredded battery cases was encapsulated for the secondary smelter operation of the General Battery Corp. in Reading, Pa. (April 1971, p 305).

In addition, the technology in a lime–fly ash–aggregate formulation has been used in several road base projects. After four years, these projects are performing as well as, or better than, the "reference" compositions.

Precisely what IU's venture plans to do with the Poz-O-Tec process was still somewhat in the formative stages at press time; its available options include:

- contract disposal of waste materials
- turn-key plant construction and operation for sludge disposal
- sale and disposal of end products
- joint ventures with other companies.

Probably, the new IU venture aims first to get the disposal business of the myriad electric utilities in the U.S., then move into areas of the chemical industry and help that industry rid itself once and for all of its irksome by-product materials. In the long term, IU looks for the opportunity of solving other industries' sludge disposal problems. SSM

Farming the forest for fiber

One way to ease the predicted shortage of wood fiber is to make better use of the trees we have

Nobody can accuse Harold Young of failing to see the forest because of the trees. Young, a professor of Forest Management at the University of Maine's school of forest resources, is determined to turn classical forest management theory around a full 180 degrees—from its preoccupation with commercially valuable large trees of a few select species to an emphasis on total fiber produced by all species of trees per acre of forestland.

Young's goal—indeed the goal of most foresters—is to increase the capacity of forests to produce useful woody fiber which can be used to make paper, hardboard, and other reconstituted wood products. There is little doubt that such effort is necessary. Extrapolations from the best available data indicate that the annual consumption of wood by the year 2000 will be 80% greater than it was in the early 1950's.

In the face of this increasing demand for wood, the nation's forests are shrinking fast. Several solutions to the problem of increasing demand coupled with diminishing raw material supply have been proposed, including recycling of waste paper, making use of plastic papers, or using fibrous plants other than trees. Among the sources of fiber frequently mentioned are bagasse—spent sugar cane from milling operations—reeds, bamboo, and kenaf. Young has even made paper from the tops of potato plants.

Kenaf has attracted considerable attention in the pulp and paper industry as a possible source of fiber. Kenaf is an annual plant which grows to maturity in months, unlike trees which may take half a century to mature. Harvesting may be done mechanically after about four months and preliminary yields have been good—about 10 tons/acre. Kenaf has been grown in Florida and Illinois—it seems to do better in the south—and responds well to soda, sulfate, and neutral sulfite pulping processes. When blended with fibers from conventional hardwood pulps, Kenaf yields papers of good brightness, opacity, and strength.

Most of the solutions to the fiber shortage that have been proposed so far are inadequate, according to Young. Plastic paper is "not appealing," Young says, because it "will add to our pollution problems." Recycling and reduction of per capita consumption of paper are "laudable, difficult to put into practice, and therefore not enough," he adds. Bagasse should be used where it's available, according to Young, and in limited geographical areas kenaf may aid in solving the shortage. Overall, however, the problem requires a more universal solution.

Fiber important

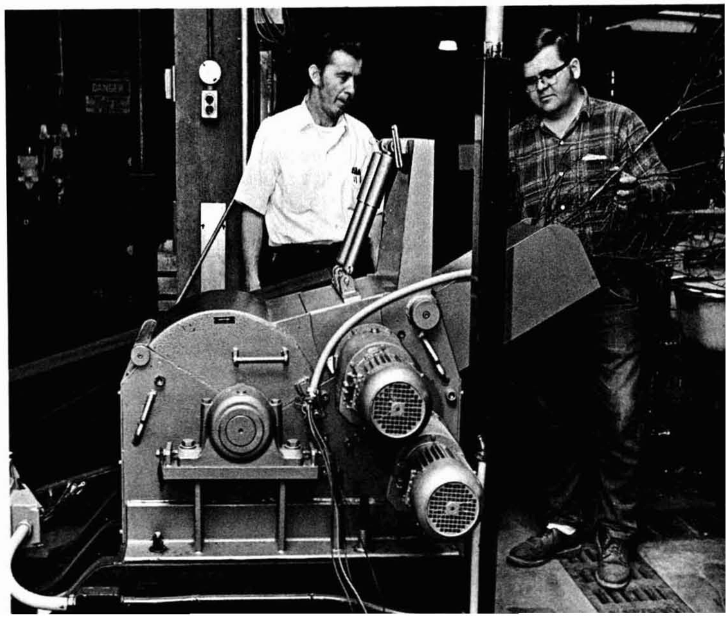
Traditional forestry is oriented toward the "merchantable bole concept" which holds that only the bole or trunk of large trees is commercially valuable. The bole is removed from the forest, debarked, chipped, and processed for fiber recovery in papermaking or building material manufacture.

But the fiber recovered from the merchantable bole is only about 65% of the total fiber content of the tree. Left behind in the stump, branches, unmerchantable top, and roots are vast quantities of potentially useful cellulose. One answer to the dwindling fiber supply would be to use the entire tree, Young says, from the "root hairs to the leaf hairs." Borrowing a cliche from the meat packing industry which uses "everything but the oink and moo," Young's "complete tree concept" advocates using "everything but the rustle of the wind through the leaves or needles of trees or shrubs."

Going himself one better, Young also proposes a "complete forest concept" which advocates reclaiming woody fiber from trees and shrubs heretofore not considered commercially valuable. And the logical extension of the complete forest concept is the introduction of woody fiber farming—cultivation, genetic improvement, and mechanized harvesting of trees and shrubs with subsequent replacement of forest nutrients removed by harvesting opera-

Puckerbrush. *Stands of young trees along rights-of-way, such as this birch grove, could provide much-needed fiber*

Klockner chipper. *Technicians feed puckerbrush to machine as the first step in claiming fiber from "weed" trees*



tions. This, Young feels, is an ecologically sound way to meet increasing demands for fiber, yet preserve the aesthetic and environmental benefits of the forest.

Young's solution to the fiber shortage involves the harvesting of "puckerbrush"—stands of noncommercial trees and shrubs which occur as successional species to the mature climax forest. In the northeast, for example, puckerbrush consists of more than 40 hardwood successional species such as gray birch, red maple, aspen, pin cherry, scrub oak, willow, and alder, which are not commercially as valuable as the climax species spruce or fir. The successional species grow rapidly and are relatively short-lived. Puckerbrush grows densely—literally thousands of stems to the acre—and it grows virtually everywhere.

Young sums up the case for using puckerbrush like this: There are probably about 25 million acres of puckerbrush in the United States. Based on his work in Maine, he concludes that fully stocked puckerbrush stands—regardless of species—produce about 1.2 tons of dry wood aboveground per year, exclusive of leaves. That's as much dry matter aboveground per acre per year as commercially valuable trees. Pulping studies based on the kraft process show that puckerbrush pulp has physical characteristics that compare favorably with those of conventional hardwood pulp. Puckerbrush chips containing bark gave a fiber yield of 41% as compared with a yield of 45% from debarked wood only of softwood species. Bleached puckerbrush pulp has a brightness of 83 compared with an industry standard of 88.

Significantly, only 30 min cooking time are required to pulp puckerbrush stems and branches—both with bark—while it takes 120 min to cook mature softwood species. The resulting savings in time and chemicals helps cut pollution.

Puckerbrush tends to have shorter fibers than mature wood, which suggests that puckerbrush would be better suited for fine and sanitary papers than for bags or wrapping papers requiring great strength.

Farming the right of way

The value of puckerbrush as a fiber source becomes readily apparent when one considers the volume that could be harvested from power line and road rights of way alone, according to Young. Rights of way are typically maintained by clearing brush, by burning or spraying, planting, and mowing grass. Costs of maintenance run from $100–200 per acre annually. But Maine bans brush burning—as do several other states—and Vermont bans the use of chemical herbicides. Where spraying and burning are not possible, maintenance costs for rights of way may increase fivefold. Young predicts that maintenance of rights of way will soar to one billion dollars annually within the next decade as burning and spraying are phased out.

With the development of suitable mechanical harvesting equipment, rights of way could be farmed for fiber. Puckerbrush areas could be cut every 10–15 years, fertilized to replace lost nutrients and allowed to grow over with puckerbrush again. Instead of a costly exercise in weed control, utilities should be able to make a small profit from the fiber produced.

Young emphasizes that knowledge of puckerbrush species is very limited. "It is entirely possible that some of these 'weed' species might turn out to be highly productive following proper fertilizing and breeding studies." Stands which are now producing slightly more than 1 ton of dry matter per acre annually might, through selective breeding and proper cultivation, produce 3–5 tons/acre/year if past successes in agriculture are any indication.

Another approach to the problem of increasing demand for fiber is known as short rotation forestry. The term refers to the shortened period of time (rotation) between establishment of a stand of trees and the harvesting of juvenile trees—a time interval which generally ranges from about 15–20 years.

Some work has been done with pine, but most of the current interest centers around hardwoods. Klaus Steinbeck and his colleagues at the University of Georgia have been growing sycamore at close spacings much as a farmer might grow corn. Mechanical harvesting of the juvenile trees on rotations of less than 10 years is followed by coppicing—the sprouting of new growths from old rootstock—which promises a sustained yield source of hardwood fiber. The "sycamore silage" crop can be mechanically cultivated, fertilized, and efficiently managed over the long term.

Other short rotation "crop" candidates are various eucalypts, poplars, sweetgum, aspen, some cottonwoods, and red alder. Young points out that puckerbrush harvesting at 10-year intervals is also considered short rotation forestry. "We're working on the same problem at different ends," he says. "Others are trying to find good species for short rotation forestry and I'm applying short rotation forestry to what we've got plenty of." HMM

Unox gets first industrial test

Lederle Laboratories is the first industrial concern to use Union Carbide's pure oxygen aeration package, and both companies are happy with the results

Lederle Laboratories, the nation's leading maker of broad-spectrum antibiotics is also on the leading edge of industrial waste treatment technology. Last July, the company dedicated a $4 million waste treatment plant at its Pearl River, N.Y., manufacturing complex, and became the first industrial user of Union Carbide Corp.'s proprietary Unox pure oxygen aeration process.

Lederle, a division of American Cyanamid, manufactures pharmaceuticals at a 500-acre plant site in Pearl River. Most of the plant's waste is spent fermentation broths produced by the microbes Lederle uses to make antibiotics. It is highly proteinaceous and contains some fats, oils, antifoaming agents, and salts. The plant effluent—some 1.1 million gpd—contains 15,000–20,000 lb BOD and 10,000 lb suspended solids (ss). Prior to construction of its Unox plant, Lederle had been treating the wastes with high-rate trickling filters before discharging to the Orangetown, N.Y., municipal sewage system.

Lederle's major problem was odor. The plant sits in a small valley, and during weather extremes, Lederle "had its own private little inversion problem," according to Charles Isberg, Lederle's Director of Community Relations. With homes less than 200 ft from the plant's perimeter, Lederle was looking for some way to control odors and treat its waste adequately and cheaply.

Enter Unox

Lederle's answer was Unox, Isberg says. The Unox process takes place in covered reactor trains, thus alleviating the odor problem. Furthermore, Unox promised improved treatment results over conventional air units with considerably less capital investment and greater control over the process. Lederle's plant has been operating for several months now, Isberg says, and the company is "very pleased" with the results.

Unox got its first full-scale test in 1970 at a 3-million gpd (mgd) municipal treatment plant in Batavia, N.Y. The test, sponsored by the Federal Water Quality Administration (FWQA) "triggered an extremely high level of interest in the Unox system," according to Union Carbide, and today there are four Unox systems onstream, five plants under construction, and 13 more for which contracts have been signed. Some 40–50 additional contracts are under negotiation, according to Carbide's Jack W. McWhirter, Unox's developer. The company is certain that it has only scratched the surface of the market.

McWhirter takes pride in the speed with which Unox was commercialized. "I don't think there's been any industrial program in the history of man that's been brought into existence and advanced as rapidly as Unox," he says with characteristic confidence. "People have been jawing about physical-chemical treatment for 10 years, and I still can't identify a single physical-chemical treatment plant that's more than a peanut curiosity," he adds.

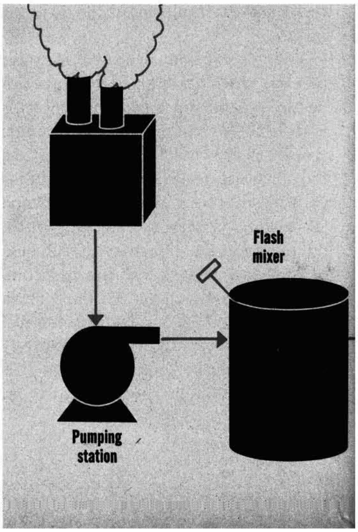
Process technology

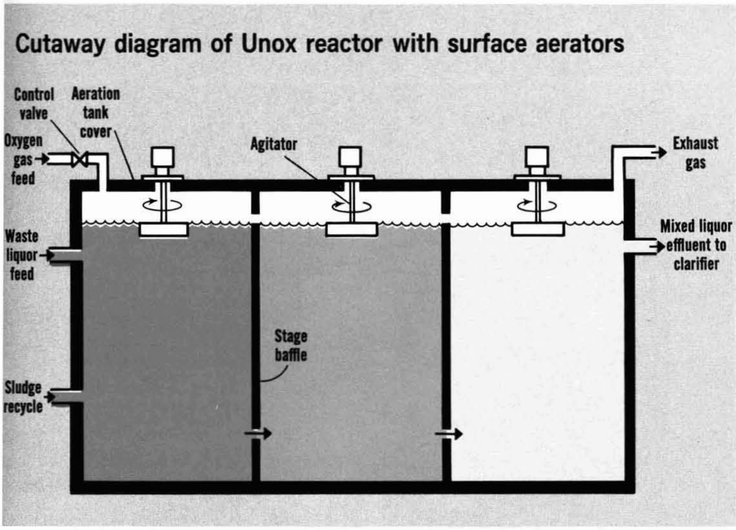
Unox is a fortuitous marriage of "recent advances in gas-liquid contacting and fluid control systems with well-established air separation and waste water treatment technology," according to Carbide.

Apart from the oxygen supply system, the workhorse of the process is the reactor—a multichambered aeration tank fitted with a gas-tight precast concrete lid. Although requirements differ for various applications, a typical reactor might have three chambers or stages—with depths ranging anywhere from 10–30 ft—separated by baffles. Waste water and oxygen are introduced into the first chamber—the oxygen filling the space between the liquid level and the tank lid—and an agitator whips up the waste to contact the oxygen. Oxygen and waste water flow concurrently through each of the three contacting stages, biological oxidation occurs, and the effluent from the third stage is settled in conventional ponds. Settled activated sludge may be returned to the first stage to be blended with raw or settled influent.

Oxygen to the system is supplied essentially on demand. As demand increases, oxygen pressure in the reactor decreases, activating a flow controller which provides more oxygen. Small amounts of surplus oxygen and waste gases such as CO_2, produced by respiring bacteria, escape to the atmosphere through a vent located above the third stage.

To a large extent, the economics of Unox hinges on an inexpensive source of oxygen (although the increased efficiency of pure oxygen compared with air allows considerable savings in land and capital construction costs). Liquid oxygen, while useful as a backup supply or in peak shaving, is too expensive to




Cutaway diagram of Unox reactor with surface aerators

use on a large scale. Plants with upward of 75-mgd nominal flow can use conventional cryogenic air separation plants. For small- or medium-volume users, Carbide's Pressure Swing Adsorption generator (PSA) fills the bill.

PSA works like this: Atmospheric air is compressed and fed to one of four adsorption columns packed with a granular material which Carbide describes only as a "molecular sieve." Air enters at the bottom of the unit and the packing preferentially adsorbs nitrogen, water, and carbon dioxide, leaving behind a nearly pure oxygen stream. The process is sequentially repeated in each of the four units. While one unit is producing oxygen, the other units are in various stages of regeneration.

The system's "pressure-swing" name comes from the fact that the adsorption process takes place in a pressurized column, and regeneration takes place when the column is depressurized to atmospheric pressure.

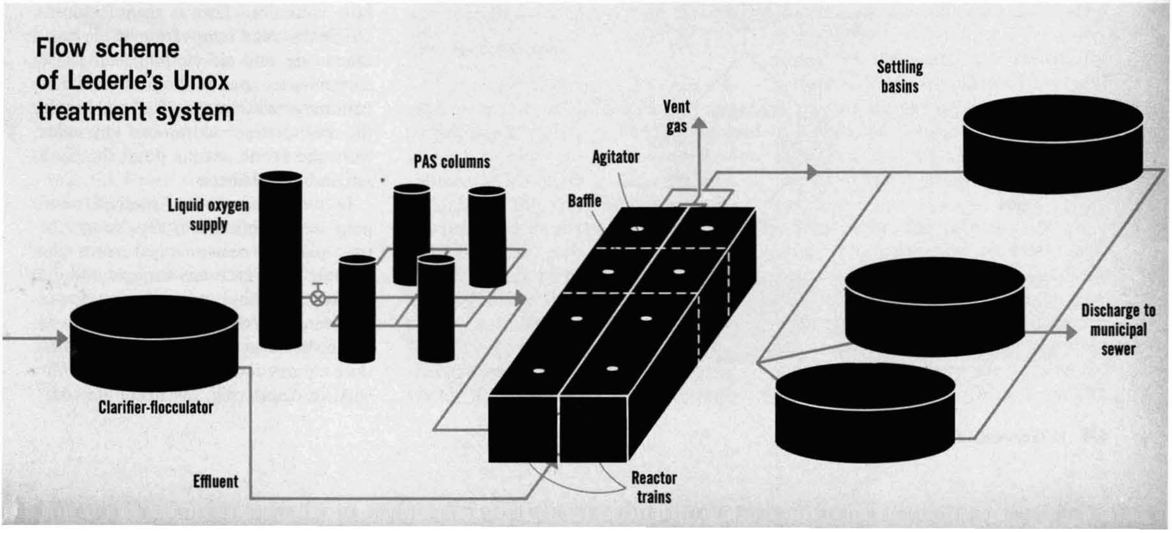
Lederle's system

At Lederle, waste from the manufacturing operation is piped to a pumping station which feeds a lime-alum flash mixer and clarifier-flocculator. Clarifier effluent, with about 50% of the BOD and 85% of ss removed, then goes to the Unox reactor for oxygen treatment. The effluent stream from the primary clarifier is split and enters two parallel Unox reactor trains. Each train consists of three contacting chambers with appropriate baffles and weirs. Each of the three chambers has a surface agitator to promote oxygen–waste water contact.

Oxygen to the system—supplied by a PSA unit with liquid oxygen backup—enters the reactor and fills the 4-ft head space above the 16 ft deep liquid. An oxygen bleed valve on the opposite end of the reactor assures the continuous flow of oxygen through the reactor trains, at pressures slightly above atmospheric. Of the oxygen that goes in, says Donald Reinhard, the microbiologist in charge of Lederle's treatment plant, about 5% escapes through the bleed as oxygen, another 5% becomes CO_2 which also escapes from the bleed, and the remaining 90% goes to make up the cells of the microbial population comprising the activated sludge. The reactor trains also feature a sludge return to recycle activated sludge to the system. Surplus sludge is dried on a Komline-Sanderson Coilfilter and composted.

Effluent from the reactor passes to a series of parallel settling basins. Clarified effluent is dumped to the sewer, virtually free of suspended solids and with a BOD reduced by about 90%, according to Reinhard.

Lederle's system features a number of extras, including provisions for ozonation and chlorination for further odor control and disinfection. "Frankly, I doubt that we will ever use them," Reinhard says. In the event its PAS oxygen generator malfunctions, a liquid oxygen supply sufficient to treat 48 hr worth of waste is on hand. A combustible gas analyzer and total organic carbon analyzer check effluent from the clarifier-flocculator before it goes to the Unox reactor, to avoid introduction of solvents used in the pharmaceutical extraction processes into the reactor trains. Effluent can be diverted to holding tanks before it enters the reactor to help shave off peaks and avoid shock loadings or poisoning of the sludge through accidental discharge of waste chemicals from the plant. HMM


Flow scheme of Lederle's Unox treatment system

Reclaiming zinc from an industrial waste stream

Cleaned up. *Five rolls of paper (right) pass through a zinc chloride bath and are bonded together to form vulcanized fiber. Until recently, wash containing zinc was discharged to Red Clay Creek (above) making it toxic to fish*

NVF Co. has built a reclamation plant which not only cleans up its discharge stream, but also provides a basic chemical for the firm's vulcanized fiber operation

Red Clay Creek, a small meandering stream in the state of Delaware, slowly winds through forests and meadows. What sets it off from most other picturesque streams is the fact that Red Clay Creek has fish living in it for the first time in 50 years.

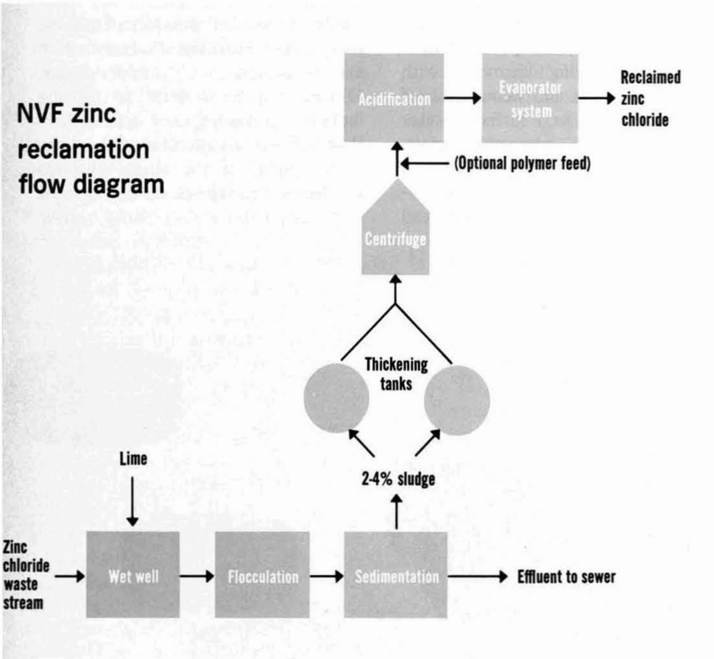
Few industries are located on Red Clay Creek; one of these is NVF Co. which has its origin in a flour mill and saw mill built in 1763. NVF manufactures 45% of the world's vulcanized fiber at Yorklyn, Del. Vulcanized fiber is a laminated plastic made from cotton cellulose paper layers bonded by chemical treatment and converted into a homogeneous material possessing unusual physical, electrical, and mechanical properties. It can be sawed, punched, drilled, milled, turned, shaved, or formed; it's available in sheets, rolls, coils, rods, tubes, or fabricated parts; and it's one of the strongest materials per unit weight known.

Vulcanized fiber

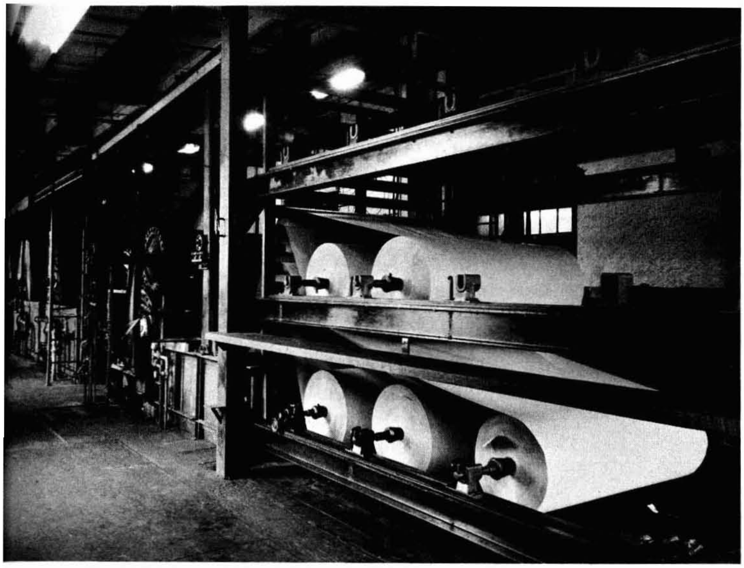
When vulcanized fiber is manufactured, zinc compounds are used in and discharged from the operation. Here's how vulcanized fiber is manufactured: Originally, rags, scraps from textile manufacturing, and old clothing—all 100% cotton—were used in the process. These cotton materials were cooked and beaten (in several steps) to remove any color from the fabric and to shred the cloth into individual fibers.

In most cases today, purified wood pulp is used instead of rags (only one NVF plant processes rags) since the availability of cotton is variable and the colored cooking wastes are serious pollutants. Wood pulp is treated in much the same manner as rags to produce a slurry containing cellulose fibers.

After dewatering, the fibers are com-



NVF zinc reclamation flow diagram



pressed into sheets of paper and wound onto large rollers. Three or more rolls of this paper are then pulled through a gelatinous zinc chloride bath which bonds the layers of cellulose paper together into a homogeneous material of desired thickness. The paper—now one layer—passes through a countercurrent washing tank (paper is pulled against the water flow) where the zinc is leached out of the vulcanized fiber.

The fiber is then dried, pressed, and ready for shipping or further processing. This cellulose vulcanized fiber is chemically pure, containing no resins or bonding agents.

The environmental problem occurs in discharging the wash water containing dissolved zinc. Vulcanized fiber has been produced at the Yorklyn, Del., location for many years; in the early years, the waste waters were discharged untreated into Red Clay Creek. Zinc is a potentially toxic substance, and fish are especially sensitive to it. For the past 50 years, the Creek was essentially sterile below the plant.

Eventually an evaporator system was built to reclaim zinc salts. Water from the washing process went through the evaporator, and zinc chloride was concentrated for reuse. However, some wash water and condensates discharged still contained zinc.

In the early 50's, Delaware officials met with NVF representatives to discuss cleaning up Red Clay Creek, but mainly in terms of wastes from NVF-owned paper mills separate from the fiber plant. NVF built an upflow clarifier that removed 80% of the BOD, reducing visible organic pollution. Effluent conformed to the state standards, but the stream was still essentially void of life.

In the late 1960's the treated and untreated discharges from the NVF fiber plant failed to meet revised state requirements for maximum acceptable zinc concentrations. The Delaware Department of Natural Resources and Environmental Control limited zinc discharges to 0.3 ppm/day if discharged directly to the stream and 1.0 ppm/day if discharged to the county sewer system.

Zinc reclamation

To meet state standards, NVF Co. began constructing a $1.2 million zinc reclamation plant, sewer, and pumping stations capable of handling one-half million gallons of waste water per day. In March of this year, the zinc reclamation plant was in full operation, handling 350,000–400,000 gpd. Waters containing 1.0 ppm zinc are pumped through an NVF-built sewer that connects with the county sewer system. The NVF sewer from Yorklyn was designed to serve simultaneously as the sanitary sewer system for the area. Last October, when the zinc reclamation plant was formally opened, NVF transmitted the title of the sewer line ownership to New Castle County. The pumping stations also will be eventually owned and operated by the county.

The zinc removal problem was a tough one, according to company officials. Little has been done in the area of zinc reclamation—only 14% of the zinc used in the U.S. today is recycled. The NVF plant was the first in the vulcanized fiber industry to undertake and succeed in removing zinc from its waste waters, says Bill Philhower, NVF division technical manager. The only other industry with similar problems is the rayon industry.

The zinc reclamation process is simple and concise: NVF chose alkaline precipitation to do the job. The basic process itself is well known, but not when applied to zinc removal.

Waste water containing 100–300 ppm dissolved zinc is brought from all points of the plant into a wet well where lime is added to control pH (8.5–9.5) and maximize precipitation. Next the precipitated zinc slurry is pumped to the zinc reclamation plant and into a flocculating chamber.

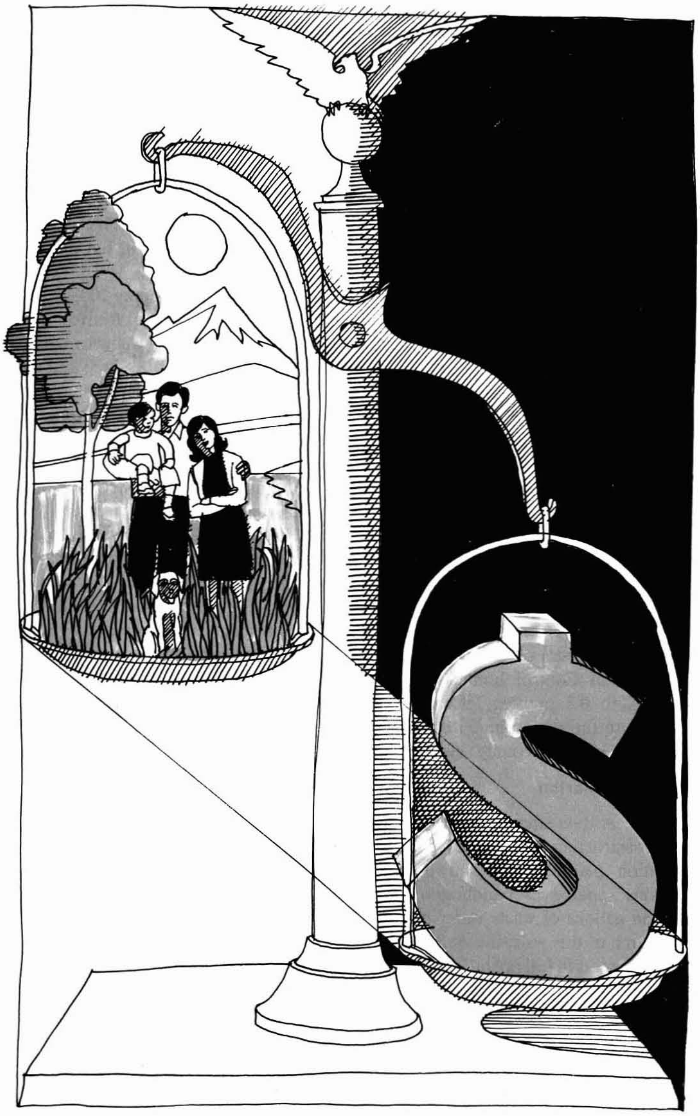
About an hour later, the slurry moves to long rectangular settling basins where the precipitated zinc salt settles as a sludge. The 2–4% sludge passes through thickening tanks.

The sludge passes from the thickening tanks through a centrifuge where polymers are added to enhance precipitation. At this point the sludge slurry is 15–25% total solids. As the sludge leaves the centrifuge, it is treated by hydrochloric acid (to acidify the alkaline solution and form zinc chloride) and is returned to the evaporator system for further concentration before it is reused in manufacturing vulcanized fiber. Liquid drawn off during the settling period is discharged to the county sewer system in concentrations well within limits set by the state.

What about the economics of recycling? The plant now recycles 50,000 pounds of zinc chloride per month for roughly the same price tag as the purchase price of fresh zinc chloride. Investment costs won't be recovered monetarily, but there are fish in the stream. CKL

EPA assesses pollution control benefits

Its Implementation Research Division is under the gun to come up with convincing facts so that the general public can be assured that the costs they are being asked to pay for controls are really worth their while in the long term



"The costs and risks of not cleaning up our environment are infinitely greater than the price of cleanup," said Council of Environmental Quality (CEQ) Chairman Russell Train, when releasing the council's third annual report. "There's no question about that in my mind, even though we are unable to put a dollar sign on the penalty, we will pay if we fail to accomplish our environmental protection goals." The need for benefit estimates was also cited in an ES&T editorial (February 1972, p 103).

Certainly, there are economists who are trying to assess the environmental benefits. In fact, a new EPA division, the Implementation Research Division (IRD), which was formed in the summer of 1971, is in the throes of assessing the benefits, at least in the air and water categories.

In the words of the director of the new division, economist Alan Carlin, the purpose of IRD is "to carry out an interdisciplinary multimedia program of studies that will help EPA implement its environmental protection responsibilities."

IRD is one of four divisions reporting to the EPA Office of Research and Monitoring under Stanley Greenfield—another is the Processes and Effects Division that Vaun Newill described to ES&T readers (July 1972, p 589). Today, IRD has approximately 20 professional staff members, more than half of whom are economists by training and experience, and operated with a $2 million budget last fiscal year (1972).

IRD consists of four branches (see box). The Economic Analysis Branch, headed by Fred Abel, is on a crash project to assess the benefits associated with pollution control, particularly water and air. Dennis Tihansky, a 1970 Harvard graduate has, for the past two years, been associated with environmental economics at the West Coast

Organizational structure

Implementation Research Division
Director: *Alan Carlin*

Economic Analysis Branch
Chief: *Fred Abel*

Ecological Studies & Technology Assessment Branch
Chief: *Edwin Royce*

Standards Research Branch
Chief: *Paul Gerhardt*

Systems Evaluation Branch
Chief: *Lawrence Ruff*

think-tank operation of the RAND Corp. Tihansky joined IRD in January and already has been deeply immersed in the benefit studies on water pollution control. He is on the firing line, so to speak, to come up with answers for a management report on the subject before the first of next year.

Tihansky tells ES&T that he has culled both the domestic and foreign literature and come up with a large collection of documents and references on the subject of water pollution control costs. Subsequently, this bibliography will be available from the Government Printing Office. It will focus on economic aspects—the cost data and cost methodology—of a wide range of pollution control strategies including direct municipal or industrial waste treatment technologies, water recycling, deep-well waste disposal, and low-flow augmentation.

Furthermore, Tihansky explains that this branch is concerned with developing methods to assess direct and indirect benefits and costs of environmental protection. It will attempt to derive benefit and cost estimates in the human health, materials, animals, vegetation, recreation, and aesthetics areas. The distribution of the costs and benefits among the population and by geographic region will also be studied, he promises. This water benefits report will include results from a project on an assessment of water pollution costs of control and damage functions.

A second project will yield a rough economic value of national damages incurred by water quality conditions in 1970. The latter item will be performed under contract. For example, one contractor (Development Planning and Research Associates, Inc., Manhattan, Kan.) will provide reports on the formulation of cost and benefit functions which measure economic effects of pollution control for various levels of water quality. A second contractor (David M. Dornbusch and Co., Inc., San Francisco, Calif.) will assess the effect of water quality levels on recreation, aesthetics, and other benefits as reflected by property values in certain areas of the U.S.

The Economic Analysis Branch is also involved in updating the widely publicized, unpublished report, "The Cost of Air Pollution Damages: A Status Report," by Larry Barrett and Thomas Waddell. Soon to be released, this report was the federal government's first systematic attempt to assess the benefits in the air pollution control category. Waddell, stationed at the National Environmental Research Center, Raleigh, N.C., is doing much of the work. Some of the work, particularly health cost, is being done under contract.

Other branches

One of the reasons for establishing the Implementation Research Division in the first place was to conduct research in ways for EPA to achieve the goals established by a maze of federal laws under which the agency operates. Each of the Division's four branches is associated more or less, with a specific priority. The Economic Analysis Branch is charged with finding ways to delineate, and quantify, the costs and particularly the benefits of pollution control.

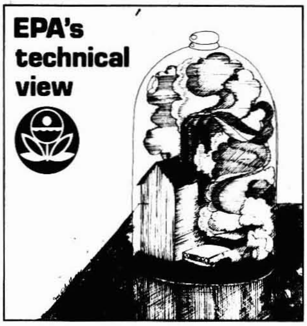
A second branch—Ecological Studies & Technology Assessment—concentrates on the research that the federal EPA needs in order to comment effectively on the environmental impact statements, the section 102 statements required by the National Environmental Policy Act (March 1972, p 209). Under section 309 of the Clean Air Amendments of 1970, EPA is charged with the responsibility of passing judgment on statements. The EPA Office of Federal Activities processes, on the average, 50–100 statements each month.

This branch also has primary responsibility for coordinating EPA's inputs into the widely published Southwest Energy Study, and last March, with the help of other EPA headquarters' offices, produced work group reports on the air and water pollution aspects of the proposed power plants in the Four Corners Area.

A third branch—Standards Research—works on the development of better methodology for evaluating environmental standards particularly for alternative approaches developed by the Economic Analysis Branch and others. This branch is headed by Paul Gerhardt, who earlier was associated with the original cost estimate of clean air on a national basis, when the Office of Air Programs was known as NAPCA in the Department of Health, Education and Welfare. Now, in his new assignment, Gerhardt and other members of this branch are looking at the net benefits of different levels of standards and different methods of implementing standards. They are giving particular attention to how standards in one media (air, water, etc.) affect pollution in the other media and to determining least cost combinations of joint (multimedia) solutions.

The last branch—Systems Evaluation—has as its main thrust the assignment of identifying incentives and related fiscal inducements to promote pollution control. In other words, how can taxes, effluent charges, subsidies, and other fiscal incentives be used to get a better quality environment with minimum costs and inconvenience to society.

As the nation moves ahead into the fourth year (1973) of the environmental decade, more will become apparent on the environmental benefits subject. SSM



New source performance standards

Feds explain air emission limitations for new plants in five industries and say another nine are on the way

Richard E. Jenkins and Gary D. McCutchen
Environmental Protection Agency,
Research Triangle Park, N.C. 27711

The Environmental Protection Agency (EPA) has determined that a rigorous approach, usually including emission testing, is necessary for the promulgation of new source performance standards. The definition of affected facilities is a critical aspect of the program; it makes easy the determination of best control, costs, and the definition of modification, as well as enhancing enforcement of the standards. Investigations to determine proposed standards involve the affected sources to ensure the integrity of the approach.

This feature outlines the concept and procedures followed in establishing performance standards for new sources and summarizes the standards that have been established to date. The Clean Air Act Amendments of 1970 triggered sweeping changes in the authority and responsibilities of the federal air pollution control program that will affect every significant source of air pollution in the nation. Major provisions of the Act are concerned with:

- controlling existing, mobile, or stationary sources of pollution to bring air quality to levels defined by the national ambient air quality standards
- setting nationwide performance standards for new or modified stationary air pollution sources
- setting national emission standards for new or existing hazardous air pollutants.

Rationale

"Standards of Performance for New Stationary Sources" are authorized in Section 111 of the 1970 Act. The overriding purpose of this section is to prevent the general occurrence of new air pollution problems by requiring the installation of the best controls during initial construction, when the installation of such controls is least expensive.

The legislative history of the Act and the law itself clearly indicate that the standards are not to be applied to existing sources by the EPA. The term "standard of performance" is defined as "a standard for emissions of air pollutants which reflects the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the administrator determines has been adequately demonstrated."

In addition, standards are to be established for "significant" sources, and for pollutants that "contribute to endangerment" of health and welfare. The administrator, for purposes of standard setting, is provided the flexibility of defining classes, types, and sizes of sources, and may revise standards from time to time. The standards must be reviewed by the National Air Pollution Control Techniques Advisory Committee.

Under the terms of the Act, source categories for which the administrator intends to set standards must first be designated in the Federal Register. After designation, and within 120 days, standards must then be proposed for public comment. After review of all comments, and within 90 days, final standards are then promulgated. If the standards are more restrictive than existing state or local regulations, the federal standards take precedence. The states can request a delegation of authority to enforce the federal standards and can enforce more stringent regulations.

A "new source" is defined as any stationary source, the construction or modification of which is commenced after the publication of proposed regulations for that source type. "Modification" is defined as any physical change in the method of operation of a stationary source which increases the amount of any air pollutant emitted by the source or which results in the emission of any air pollutant not previously emitted.

It is beyond the scope here to explain

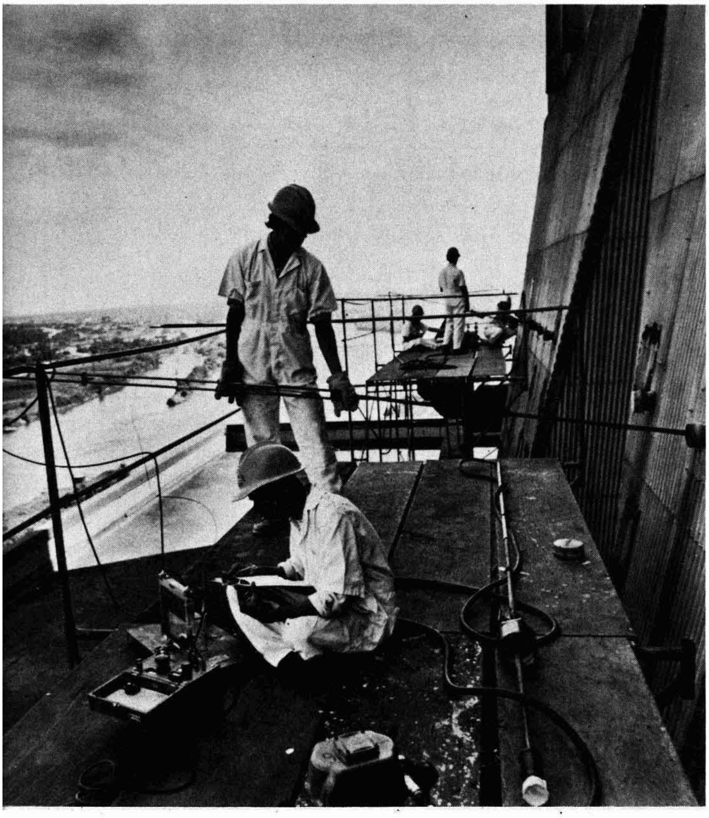
or analyze the many decisions made by EPA in the process of developing standards of performance. A brief summary of the more pertinent concepts is necessary, however, to provide an understanding of the standard setting process.

EPA's interpretation

Best system of emission reduction. In the judgment of EPA, Section 111 of the Act mandates best control, as opposed to normal, conventional, or good control. By definition, EPA is not attempting to define averages or representative emission rates. As a result, the available data as a justification for a standard will be limited to emission tests of a relatively small number of facilities.

Cost of control. Congress has determined that it is in the best interests of the Nation to apply the best systems of emission reduction on new sources. Consideration of cost, therefore, is applied as a modifier to avoid extremes.

Adequately demonstrated. If possible, it is the intention of EPA to establish standards that can be achieved by more than one control system including, as necessary, foreign technology. This criterion is, however, not absolute. Indeed, the term is broadly interpreted to include a range of secondary considera-



ESP testing. *Technicians take samples from power plant stacks to verify electrostatic precipitator design efficiency*

EPA and testing contractors visited these plants

Steam generators tested

Duke Power	Pelzer, S.C.
Detroit Edison	Trenton, Mich.
Illinois Power	East Alton, Ill.
Hartford Electric	Middletown, Conn.
Allegheny Power	Morgantown, W.Va.
Kansas Power and Light	Lawrence, Kan.
Liquid Carbonic	Seattle, Wash.
United Illuminating	Bridgeport, Conn.
Union Electric	Labadie, Mo.
Union Carbide	Alloy, W.Va.
Southern California Edison	Los Angeles, Calif. (two units)

Incinerators tested

Dade County incinerator	Dade County, Fla.
Municipal incinerator	Chicago, Ill.
Municipal incinerator	New York, N.Y.
Municipal incinerator	Kessel, West Ger.
Municipal incinerator	Stockholm, Sweden
N. W. incinerator	Miami, Fla.

Portland cement plants tested

Maule Industries	Miami, Fla.
Ideal Cement	Tijeras, N.Mex.
Ideal Cement	Seattle, Wash.
Ideal Cement	Castle Hayne, N.C.
Dragon Cement	Northampton, Pa.
Ideal Cement	Houston, Tex.
Idaho Almaden	Weiser, Idaho
Oregon Portland Cement	Lake Oswego, Ore.
Giant Cement	Harleyville, S.C.

Nitric acid plants tested

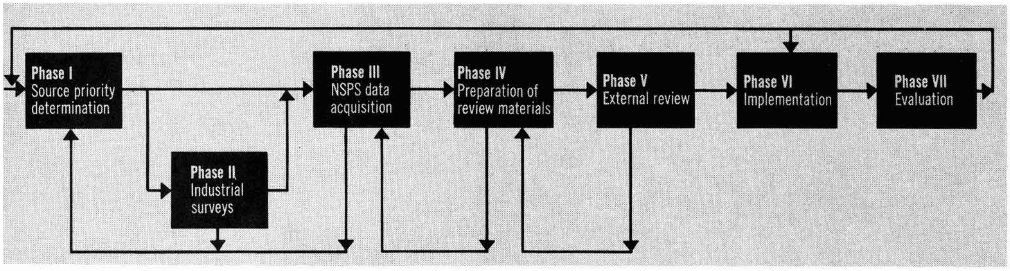
Hercules	Donora, Pa.
Shell Chemical	Ventura, Calif.
Shell Chemical	St. Helens, Ore.
Collier Chemical	Brea, Calif.
Du Pont Chemical	Gibbstown, N.J. (three tests)
Brockville Chemical	Brockville, Ont.

Sulfuric acid plants tested

American Cyanamid	Linden, N.J.
Olin Chemical	Paulsboro, N.J.
Allied Chemical	Elizabeth, N.J.

FIGURE 1

Standard setting procedure



tions, including results of pilot plant or prototype installations, technology transfer from one source category to another, and engineering judgment.

Affected facility. Many sources emit pollutants from more than one process stream. In such cases, the pollutants emitted, the availability of control systems, and the definition of modifications are variable. For these reasons, standards will often be established for specific components as opposed to an entire source installation. This approach is authorized by the Act, since the administrator can differentiate between types, sizes, and classes of sources. The use of this concept is also an aid to enforcement of the standards.

Source modification. To date, definition of this term beyond the general words of the Act has been done by exception. Upon promulgation of a first set of standards in December 1971, the following have been excluded: routine maintenance, repair, and replacement; increase in production rate up to design capacity; increase in hours of operation; and the use of alternative fuels or raw materials, provided such alternatives were considered in the original design.

Implementation. Full implementation of Section 111 occurs in seven phases, starting with the determination of priorities and ending with an evaluation of effectiveness, which serves as feedback (Figure 1).

Analysis

Phase I of the system involves a general analysis of available control technology, cost of control, emission rates, growth, source location, and

Table 1

Emission improvement required and costs resulting from performance standards

	EMISSIONS		COST OF ADDED CONTROL, %		
Source category	**Existing installations**	**NSPS**	**Investment**	**Operating**	**Affected size**
Fossil fuel–fired steam generators	(lb/10^6Btu)	(lb/10^6Btu)			Over 250 million Btu/hr heat input
Particulates	0.04–4.0	0.1	3[a]	0.01¢/kW hr[a]	
Sulfur dioxide					
Liquid fuel	3.0 (av)	0.8	10[b]	7–30[b]	
Solid fuel	5.0 (av)	1.2	12[a]	0.12¢/kW hr[a]	
Nitrogen oxides					
Gaseous fuel	0.4 (av)	0.2	5[b]	4[b]	
Liquid fuel	0.7 (av)	0.3	7[b]	4[b]	
Solid fuel	1.4 (av)	0.7	1[a]	0.01¢/kW hr[a]	
Visible emissions		#1 Ringel. or 20% Op.			
Incinerators	(gr/SCF)	(gr/SCF)	9–15[b]	. . .[c]	Over 50 tons/ day charging rate
Particulates	1.0	0.08			
Portland cement			12[b]	5–7[b]	
Particulates	(lb/ton feed)	(lb/ton feed)			None
Kilns	45	0.3			
Clinker coolers	30	0.1			
Visible emissions					
Kilns		#$^1/_2$ or 10% Op.			
Others		<10% Op.			
Nitric acid	(lb/ton acid)	(lb/ton acid)	4–8[b]	0–2[b]	None
Nitrogen oxides	43	3.0			
Visible emissions		<10% Op.			
Sulfuric acid	(lb/ton acid)	(lb/ton acid)	14–38[a]	0	None
Sulfur dioxide	22–85	4			
Acid mist	0.4–0.9	0.15			
Visible emissions		<10% Op.			

[a] Costs from Federal Register (37 FR 55), March 21, 1972.

[b] Costs from Background Information for Proposed New Source Performance Standards.

[c] For refractory wall, $29,000/year for 100-ton unit; $65,000/year for 300-ton unit. For water wall, $13,000/year for 100-ton unit; $23,000/year for 300-ton unit.

Table 2

Emission test details

Source category	Control equipment	Units tested	NUMBERED SAMPLES TAKEN Part	NO_x	SO_2	F	Hg	HCl	Metals	CO
Fossil fuel-fired steam generators	Electrostatic precipitators Limestone scrubbers	12	60	136	54	14	25	10	7	...
Incinerators	Electrostatic precipitators Scrubbers	6	38	42	12	...	12	13	22	3
Portland cement	Baghouses Electrostatic precipitators	9	57	53	9	...	6	...	17	...
Nitric acid	Catalytic decomposition	8	...	75	...	...	...	...	...	6
Sulfuric acid	Dual absorption	3	15	...	12	...	...	...	...	...

Emission testing contractors

Contractor	Contact
Monsanto Research	W. H. Hedley
Environmental Engineering	J. B. Koogler
Resources Research	R. Allen
Cottrell Environmental	G. H. Kelly
Scott Research Laboratories, Inc.	N. Troxel
PEDCo Environmental	R. Gerstle
Midwest Research	P. C. Constant
Rust Engineering	D. P. Meffert
York Research Corp.	A. Licata
Valentine, Fisher & Tomlinson	W. Snowden
Walden Research	A. Doyle
Battelle Columbus	R. Engdahl
Roy F. Weston	F. Cross
Engineering Sciences	M. Lukey

Table 3

Nine source categories under consideration

Source category	Pollutants to be considered[a]
Primary nonferrous smelters	A,P,S
Aluminum reduction plants	F,H,P,S
Kraft paper mills	P,T
Gas turbines	C,H,N,P
Coal cleaning plants	P
Phosphate fertilizer plants	F
Ferro-alloy plants	P
Secondary aluminum smelters	Cl,F,P
Electric arc steel furnaces	P,S

[a] A = Acid mist, C = carbon monoxide, Cl = chlorides, F = fluorides, H = hydrocarbons, N = nitrogen oxide, P = particulate matter, S = sulfur oxide, T = total reduced sulfur.

existing regulations (state, local, and federal), for both sources and pollutants. EPA policy and regulatory efforts for water and land pollution are important inputs to this analysis.

In many cases, available data does not lend itself to firm analysis. For these situations, industrial surveys (Phase II) are recommended to provide the necessary information. When sufficient data are available, either with or without a detailed industrial survey, a program is initiated to acquire specific documentation of emission from best control systems, leading to recommended standards (Phase III). Contact with the sources, trade associations, and consultants represents a major factor of Phases II and III. Given an adequate data base, appropriate documentation and analysis of issues is completed (Phase IV), followed by review within EPA and by other groups, culminating in a promulgated standard (Phase V). Implementation then follows (Phase VI), followed by evaluation (Phase VII), and, if necessary, the establishment of priorities for revision (Phase I).

To date, EPA has promulgated standards of performance for five source categories: fossil fuel-fired steam generators, municipal incinerators, Portland cement plants, nitric acid plants, and sulfuric acid plants (Table 1). Table 2 contains additional data on emission

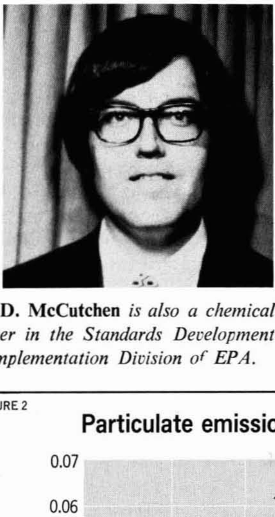
Table 4

Particulate emission data for steam generators

Net, MW	Output (10^6 Btu)	Excess air, %	AV EMISSIONS USING EPA METHOD 5 (gr/DSCF)	(lb/10^6 Btu)	Control device	Collector area, ft^2/ACFM	Fuel and boiler type
100	900	18.2	0.179	0.330	Hot-side ESP	...	Coal[a]
540	4800	32.7	0.084	0.169	Cold-side ESP	0.1790	Coal[b]
400	3600	33.6	0.060	0.131	Cold-side ESP	0.1617	Coal
550	5100	29.8	0.050	0.105	Cold-side ESP	0.1698	Coal
125	1100	59.0	0.074	0.213	Scrubber[c]	...	Coal
625	5600	43.15	0.145	0.308	Cold-side ESP	0.3309	Coal
50	500	64.8	0.0275	0.047	Cold-side ESP	0.3823	Coal
30	300	48.5	0.037	0.066	Hot-side ESP	0.4217	Coal
110	990	34.0	0.033	0.070	Cold-side ESP	0.1260	Oil
350	3200	12.8	0.085	0.145	Cold-side ESP	0.1825	Oil

[a] Tangentially fired.
[b] Corner-fired.
[c] Limestone injection followed by wet scrubber.
[d] Front-fired.
[e] Horizontally front-fired.

Richard E. Jenkins *is a chemical engineer in the Standards Development and Implementation Division of EPA. Address inquiries to Mr. Jenkins.*



Gary D. McCutchen *is also a chemical engineer in the Standards Development and Implementation Division of EPA.*

tests of these source categories. Industrial studies have been conducted, as well as special tests to acquire data for additional standards. A list of sources that are under investigation, as well as estimates of future possibilities, is available (Table 3).

Data acquisition

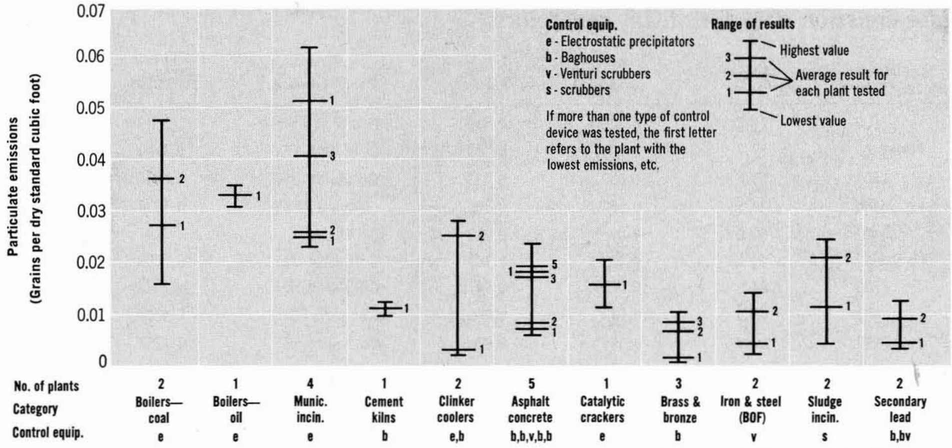
After a source category has been selected, data are accumulated to quantify emission rates, usually by source tests of effluents from well-controlled facilities. Utilizing such resources as technical societies, trade associations, equipment manufacturers, and personal contacts, a list of plants is recommended as having well-controlled processes. If there are several methods of control, examples of each are selected. An inspection is made to verify the type of control equipment in use, to assess its efficiency and reliability, to request information on the costs involved with its installation and use, and to judge the suitability of the equipment for source testing. Most tests are conducted by contractors with EPA engineers observing the testing process. Copies of the test data are sent to the management of the plant tested. While the testing program is in progress, data on the economic impact of control are assembled, and a technical report for each standard is compiled to accompany the proposed standard. During the development of the standards, the raw data are available for review and discussion, on request.

An example which helps to clarify many aspects of data acquisition is the information generated to justify a standard for particulate matter from fossil fuel–fired steam generators. In this case, a total of 10 boilers were tested, including two coal-fired industrial boilers, two steam-electric units burning fuel oils, and six coal-fired steam-electric units. All but one of these units were equipped with electrostatic precipitators of reportedly high removal efficiencies. The exception utilized a marble-bed scrubber which removed both particulate and sulfur dioxide via lime slurry. Both cold-side and hot-side electrostatic precipitators were tested. The data (Table IV) indicates, to a certain degree, the range of emission rates that can be expected even after a relatively stringent selection process has been followed. Determination of a final standard is, of course, complicated by such variation, and will become more difficult as priorities change from known to unknown sources. To a certain degree, this complexity justifies the need for specific standards for specific sources.

Further support for this concept is provided by comparing measured emissions from well-controlled plants for a variety of source categories (Figure 2). A wide range exists, at the present time, between well-controlled emission rates for one source as opposed to another.

FIGURE 2

Particulate emissions—NSPS tests

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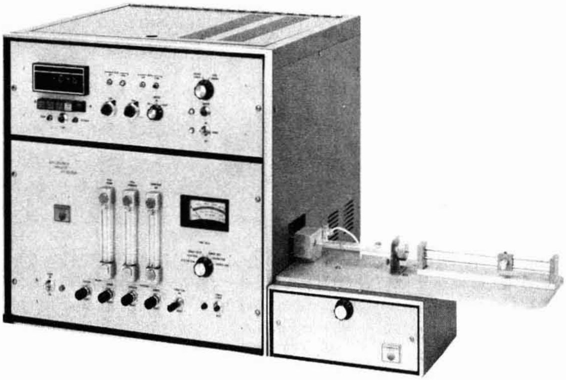
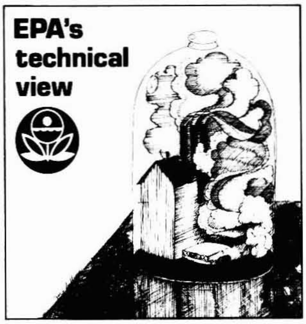


Thomas R. Hauser and
Carl M. Shy

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



Position paper:

On July 27, 1972, William D. Ruckelshaus, Administrator of the Environmental Protection Agency, deferred implementation of regulations regarding the control of nitrogen oxides (NO_x) from certain stationary sources from July 31, 1972 to July 1, 1973. The decision to postpone the applicable regulation for one year was dictated by a need to reassess and, where necessary, revise the Administrator's classification of Priority I Air Quality Control Regions (AQCR) set forth on May 31, 1972 (Federal Register 37:10842). The need to reassess was in turn predicated on the results of recent EPA studies which indicated that the reference method for measuring nitrogen dioxide (NO_2) in ambient air (Federal Register 36:8200, Apr. 30, 1971) seems to possess inherent deficiencies which may have caused an overestimation of the extent of the NO_2 problem in various AQCR throughout the United States.

As a result of the above, EPA has received numerous inquiries into the current status of NO_2 measurement methodology. This article presents an up-to-date status report on the above subject and explains the actions within EPA which are under way to resolve the various questions which have been raised.

The 1967 amendments to the Clean Air Act required the Secretary of Health, Education and Welfare to develop and publish air quality criteria which, in his judgment, were required for the protection of the public health and welfare. Additionally, the Act called for the establishment of Air Quality Control Regions (AQCR) based on jurisdictional boundaries, urban-industrial concentrations, and other factors including atmospheric areas, necessary to provide adequate implementation of air quality standards. Two hundred forty-seven AQCR were designated between June 1968 and January 1972. "Air Quality Criteria for Nitrogen Oxides" was published in January 1971.

The Clean Air Act was further amended in 1970 (PL 91-604) and required the administrator of EPA to establish, among other things, National Ambient Air Quality Standards, National Emission Standards for Hazardous Air Pollutants, and Standards of Performance for New Stationary Sources of air pollution. The administrator promulgated National Ambient Air Quality Standards for six pollutants, including NO_2, on Apr. 30, 1971. Concurrently the analytical methodology or measurement principle to be used to measure the six pollutants was promulgated, and these methods were called the "reference methods." "Requirements for the Preparation, Adoption, and Submittal of Implementation Plans" was published on Aug. 14, 1971, which outlined for the States what was to be included in plans to implement or achieve the National Ambient Air Quality Standards. These regulations included specifications that pollutants be measured by the published reference method or a method demonstrated to be equivalent to the reference method.

Reference method

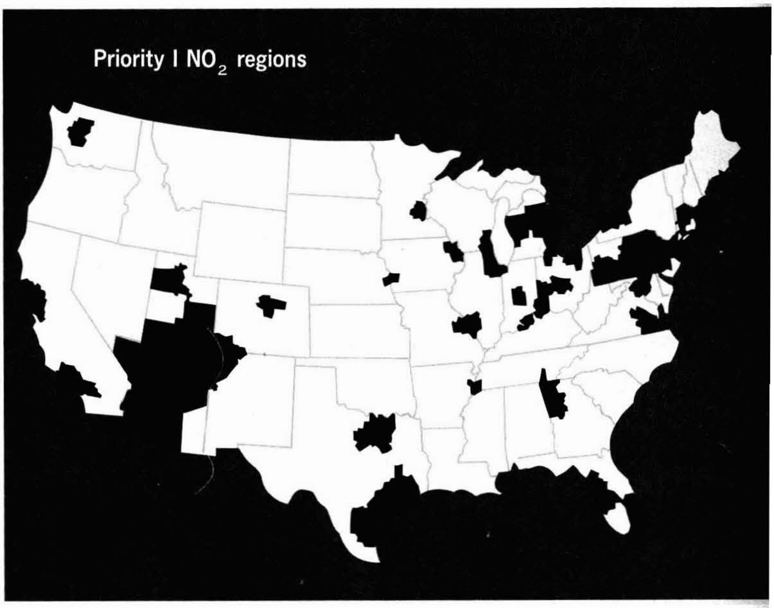
The reference method for the analysis of NO_2 in ambient air to determine compliance with the national air quality standards is the Jacobs-Hochheiser procedure as modified by chemists within the National Air Surveillance Networks (NASN). This method involves the collection of NO_2 by bubbling ambient air for a 24-hr period through an aqueous $0.1N$ sodium hydroxide solution to form a stable solution of sodium nitrite. The nitrite ion formed in the absorbing reagent is then reacted with sulfanilamide and *N*-1-naphthylethylenediamine in acid media to form an azo dye which is measured colorimetrically at 540 nm. Calibration of the method is achieved in accordance with directions published along with the reference method using standard nitrite solutions. The collection efficiency of the reference method for NO_2 was previously determined to be 35% and a correction for this efficiency has been applied to all data gathered to date utilizing the reference method. It is precisely this average collection efficiency correction factor that is now in question, and this subject will be addressed later in this discussion.

In the summer of 1971, EPA conducted a special study in urban areas with potential air pollution problems to gather ambient NO_2 data to be used by the states to develop implementation plans for the control of NO_x. The method used in the 1971 Summer Study was the reference method as published in the *Federal Register*. As a result of that

Doubts about the accuracy of measured concentrations of NO_2 in ambient air have led EPA to reassess both the analytical technique and the extent to which NO_x control will be needed to satisfy federal law

NO_x measurement

Summer Study and other available data, 45 AQCR in 29 states were classified as Priority I for NO_2—that is, these states may be required to control NO_x emissions from stationary sources to have acceptable implementation plans. Concurrent with the Summer Study, intensive investigations were being conducted by scientists at the National Environmental Research Center in the Research Triangle Park, N.C. (NERC-RTP) to reinvestigate the analytical parameters of the reference method. These investigations resulted in EPA arriving at its present position as stated earlier—i.e., that the results of recent investigations indicate that the reference method for NO_2 seems to possess inherent deficiencies which may have caused an overestimation of the extent of the NO_2 problem in the various AQCR. It should be noted that EPA has already established the regulatory framework necessary for the control of NO_x based on the original data and, hence, control can proceed quickly if warranted by the new data. On the other hand, the one-year delay in the application of control regulations has been instituted by EPA to ensure that final control regulations are consistent with the findings of the new data.



Recent investigations

The main investigations leading to the conclusion that the reference method may have some inherent problems were conducted by the Office of Measurement Standardization (OMS) and the Laboratory Measurements Research Section (LMRS) of the Division of Chemistry and Physics and in the Air Quality Analytical Laboratory (AQAL) of the Division of Atmospheric Surveillance. Nitrogen dioxide generation–dilution systems based on an NO_2 permeation tube were used during all investigations. Nitrogen dioxide–air mixtures of varying concentrations were generated by the OMS and the mixtures were sampled and analyzed by the reference method for NO_2. The collection efficiency of the reference method was then determined by comparing the amount of NO_2 found after analyses vs. the known amount of NO_2 generated and introduced into the sampling train. Before insertion of the permeation device in the NO_2 generation–dilution apparatus, dynamic blanks were run, and it was found that blank corrections were negligible.

For each test atmosphere generated, at least five simultaneous samples were collected and analyzed. Hence, the data points in Figure 1 are averages $\geq$ five determinations. Additionally, four different permeation devices were used during the study. The results shown in Figure 1 demonstrate that the collection efficiency of the reference method varies nonlinearly with NO_2 concentrations from 15% at 740 $\mu g/m^3$ to 50–70% at the 20–50 $\mu g/m^3$. These data agree reasonably well with the limited permeation tube data published in the reference method and by Purdue et al. [ES&T, **6,** 152, (1972)]. This method of calibration differs from that published for the reference method in that NO_2 gas rather than nitrite ion is dynamically carried through the reference procedure. This, in turn, reflects the advancement in the state of the art and use of the NO_2 permeation device as a calibration standard which afforded the opportunity to study the NO_2 analytical problem in much more depth.

The second problem recently found in the reference method is a positive interference caused by the presence of nitric oxide (NO) in the ambient atmosphere. Dilute mixtures of known concentrations of NO_2 in air were prepared by passing purified air over an NO_2 permeation tube. Known amounts of NO were then metered into the dilute NO_2 gas stream, and the entire mixture was analyzed by the reference method for NO_2. The response obtained from the reference method, with and without NO in the dilute NO_2 gas stream, was noted and results appear in Table I.

The reference method as published contains directions on how to calculate the concentration of NO_2 ($\mu g/m^3$ and ppm) in the air sampled. In these calculations a correction is included for the overall efficiency of the method which historically had been determined to be 35%. Inspection of Figure 1 shows that at low concentrations of NO_2 in the atmosphere (30–60 $\mu g/m^3$), where collection efficiencies are much higher than 35%, the reported concentrations of NO_2 will be much higher than the actual ambient level. The positive interference from NO, the extent of which still needs further evaluation, could also be important in these areas of low concentration. In areas where the ambient level of NO_2 is above 120–130 $\mu g/m^3$, a 35% collection efficiency factor is approximately valid; at higher atmospheric concentrations, the application of the 35% correction factor will underestimate the actual NO_2 concentration in the air sampled.

Validity of past data

EPA fully recognizes that the validity of a tremendous amount of data collected in previous years may now be in jeopardy. This is especially true for the lower ambient air concentrations of NO_2 which may be erroneously high because of the collection efficiency factors or NO interference discussed earlier. Where data have been used not simply for trend monitoring but in decision-making processes for control of stationary sources, the validity of the data becomes all important.

One way to validate the past data is to apply a true correction factor to the data, if possible, to make them valid. To ascertain if a true correction factor can be generated, it will be necessary to demonstrate a consistent relationship between the current reference method and another analytical technique. If a consistent relationship can be shown, then a correction factor can be applied; if it cannot, then a new reference method should be adopted.

To this end, the Division of Atmospheric Surveillance (DAS) and the Division of Health Effects Research (DHER) of NERC-RTP have added projects to ongoing activities to determine the interrelatability of existing NO_2 methodology. In conjunction with NASN activities, DAS is investigating two other new 24-hr integrated methods at all 200 sampling stations on the NASN network in addition to the current reference method now in use. A third new method will be added shortly. In addition, DAS is installing chemiluminescent equipment at the Continuous Air Monitoring Program (CAMP) sites. This means that at each CAMP site, NO_2 will be concurrently measured by an instrument based on the continuous Saltzman method, by a chemiluminescence instrument, and three or four 24-hr integrated methods employed by NASN.

Similar studies are being conducted by DHER in conjunction with its health effects studies in Los Angeles, Calif., Chattanooga, Tenn., and St. Louis, Mo. In these cities, six 24-hr integrated methods, a continuous Saltzman instrument, and a chemiluminescence instrument are concurrently measuring NO_2 in the ambient air.

When all the studies are completed and the data are evaluated, the results will be published. At that time, the decisions will be made concerning the validity of past NO_2 data collected by the current reference method. The new decisions, if needed, concerning the reclassification of AQCR will be made early in 1973.

Another facet of this method evaluation and comparison study is that the data generated will additionally assist EPA in making decisions in the area of equivalent methods mentioned earlier. Guidelines for the demonstration of equivalency of analytical methodology are being developed by EPA with tentative publication scheduled for later this year.

Effect on stationary source decisions

The classification of AQCR with respect to NO_2 was accomplished in November 1971. The determination of whether an AQCR had an NO_2 problem of such magnitude to require stationary source NO_x reduction was based in part on air quality data collected by the reference method. At the present time, some 45 AQCR in 29 states are classified as Priority I for NO_2 and may require that controls be placed on stationary sources. The sources to be controlled include oil- and gas-fired steam generating plants of more than 250 million Btu/hr of heat input and nitric acid plants. If the deficiencies in the reference method are further substantiated, it must be con-

FIGURE 1

Response to NO_2 reference method

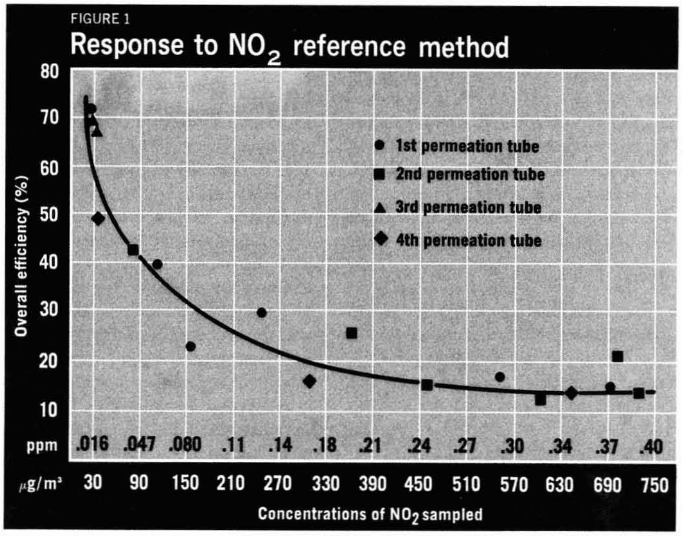


TABLE I

Effect of NO on the Reference Method for NO_2

μg/m³				
NO_2	NO	Ratio, NO/NO_2	Expected NO_2 recovered, %	Apparent NO_2 recovered, %
100	0	0.0	39	38
102	63	0.6	39	38
105	127	1.2	38	52
122	627	5.1	36	57
189	0	0.0	29	29
244	1205	4.9	24	45
248	1279	5.2	23	55
215	1242	5.8	26	50
311	0	0.0	20	17
316	111	0.4	20	30
318	332	1.1	20	33
356	1060	3.0	18	44

TABLE II

Calibration of the Reference Method as Used in Chattanooga

No. of replicates	NO_2 introduced, ppm	NO_2 found, ppm	Overall efficiency, %
20	1.00	0.135	13.5
31	0.50	0.090	18.3
26	0.10	0.039	39.0
44	0.056	0.020	35.0

TABLE III

Computed NO_2 Concentrations, ppm

No. of samples	Site No.	Arith. mean constant collection efficiency	Arith. mean variable collection efficiency	Upper & lower 95% limits for column 4
65	School 1	0.109	0.167	0.141, 0.193
65	School 2	0.078	0.097	0.085, 0.109
65	School 3	0.062	0.069	0.061, 0.078

cluded that some of the AQCR with reported NO_2 problems may not truly have an NO_2 problem but only one resulting from the inadequacies of the reference method. Hence, the EPA decided to defer application of the promulgated regulations to July 1, 1973. To generate data to assist in making the future decisions, the DAS is placing three or four 24-hr integrated methods in addition to the reference method in all 200 NASN sites as previously stated. One 24-hr integrated method has been running concurrently with the reference method at all NASN sites since January 1972 and a chemiluminescent instrument to monitor NO_2 is being placed in every AQCR classified as Priority I. These monitoring activities coupled with the activities given earlier in the paper will enable the Stationary Source Pollution Control Program to reevaluate their classification of AQCR for NO_2 based on the best-accepted state of the monitoring art.

Effect on mobile sources of NO_2

In Section 202, Title II "Emission Standards for Moving Sources," of the Clean Air Act as amended in December 1970, it is specifically stated: "The regulations under subsection (a) applicable to emissions of oxides of nitrogen from light-duty vehicles and engines manufactured during or after model year 1976 shall contain standards which require *a reduction of at least 90 per centum from the average of emissions of oxides of nitrogen actually measured from* light-duty vehicles manufactured during model year 1971 which are not subject to any Federal or State emission standard for oxides of nitrogen" (emphasis added). Two points need emphasis. The reference method for NO_2 as published is applicable to ambient air and not emission sources. Second, the law calls for a 90% reduction in the average emissions *actually measured* in 1971. The methodology used in 1976 should be equivalent to that used in 1971 to measure the NO_x emission initially. Since the analytical method used for NO_x from mobile sources in 1971 was *not* the reference method for ambient air, then the newly recognized deficiencies in the reference method should have *no* effect on the measurement of NO_x emissions from mobile sources.

Effect on national primary NO_2 standard

As mentioned earlier, NO_2 measurements by the reference method cannot be assumed to have a constant 35% overall efficiency. Since this assumption was made for NO_2 measurements obtained using the reference method as modified for the Chattanooga School Children Study [Shy, C. M., et al., *APCA J.*, **20,** 539 (1970)], a reexamination of the data is required. For this purpose, NO_2 concentrations obtained in Chattanooga during the 1968–69 health study were compared with NO_2 measurements obtained by the U.S. Army, which operated continuous monitors based on the Saltzman technique. These monitors ran simultaneously within 0.4 mile of one of the air monitoring stations established in the high NO_2 exposure area for the health study (School 1 of the Chattanooga School Children Study). The results of these measurements obtained from November 1968 through April 1969 (the period of the EPA health study) were as follows:

U.S. Army instruments (Saltzman method), ppm		EPA health study (reference method), ppm
Number 1	Number 2	
0.099	0.087	0.109
0.093 (av of 1 and 2)		

These data show relatively close agreement between the two methods. EPA results are 17% above U.S. Army values. The two methods provide independent estimates of the population exposure on which our primary national standard was based. The close agreement supports the existing national primary standard for NO_2.

In addition, the daily NO_2 concentrations obtained during the EPA health study were reevaluated to account for the variable collection efficiency of the method used during the Chattanooga study. The analytical procedure was dynamically calibrated using an NO_2 permeation device, and the results are given in Table II. From the data given in Table II, it is possible to construct a calibration curve by plotting NO_2 introduced on the Y axis vs. the overall amount of NO_2 found on the X axis. Using a regression analysis, a 95%

confidence band was then placed around this calibration curve. Then, to correct the Chattanooga data for the variable collection efficiency, the results of the individual daily analyses were rectified from NO_2 concentrations found to true NO_2 concentrations by use of the introduced/found ratios given in the calibration curve. At the same time, the corresponding upper and lower 95% confidence limits were also obtained for each individual value. This procedure was followed for each of the three "high NO_2" stations in the Chattanooga study and the results are given in Table III. Column 3 in Table III is the arithmetic mean of the various individual NO_2 concentrations incorporating a constant 35% overall efficiency; column 4 was developed using the procedure described above to correct for the variable collection efficiency.

These revised estimates must be qualified for values found at School 3 in the high NO_2 area. Most of the individual values in this area were below 0.015 ppm which was the lower limit for calibration data. Corrected NO_2 concentrations for these values were computed by extrapolating the calibration curve data beyond the lower limits of observed introduced/found ratios. However, the results given in the above tabulation represent reasonable best-judgment estimates based on these extrapolations.

Our revisions, based on corrections for variable collection efficiency, increase by 11.3% the estimate of NO_2 exposure at School 3, the neighborhood at which a significant excess of acute respiratory illnesses was observed at the lowest of the three high NO_2 area exposures.

The U.S. Army also collected NO and NO_2 data by the continuous Saltzman method at six sampling sites in Chattanooga during 1967 and 1968. Two of these sites were located in the high NO_2 exposure area of the Chattanooga health study. A comparison of means of hourly NO and NO_2 data is given below:

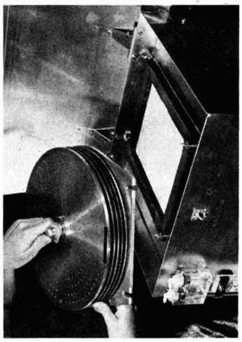
	Arithmetic mean, $\mu g/m^3$		
	NO	NO_2	NO/NO_2
Site A	135	394	0.38
Site B	98	263	0.37

Inspection of the data demonstrates that the ratio of NO to NO_2 in the air of the high NO_2 exposure area is about 0.38. When this ratio is compared with the data available in Table 1, it is seen that at low NO_2 concentrations (approximately 100 $\mu g/m^3$) the NO/NO_2 ratios observed in Chattanooga would have little effect on the apparent collection efficiency of NO_2. At higher NO_2 concentrations, the NO/NO_2 ratios would increase the apparent collection efficiency from approximately 20 to 30%.

In conclusion, the several independent methods available to estimate NO_2 exposure during the Chattanooga health study do not support a revision of the National Air Quality Standard for NO_2.

Thomas Hauser *is the deputy director of EPA's Atmospheric Surveillance Division. He has been with federal air pollution control agencies for the past 17 years and has published widely in the field of methodology for analysis of air pollutants. Address inquiries to Dr. Hauser.*

Carl Shy *is the director of EPA's Health Effects Research Division. Dr. Shy has served with the U.S. Public Health Service and NAPCA and holds teaching positions at the University of North Carolina and Duke University. He is an editorial consultant for the* Journal of Chronic Diseases.



Corona Discharge Oxidation of Sulfur Dioxide

Michael J. Matteson,[1] Hugh L. Stringer,[2] and Walter L. Busbee[3]
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Ga. 30332

■ Sulfur dioxide (500–3000 ppm) in a flowing humid air mixture was exposed to a corona discharge in a wire-to-cylinder reactor. Sulfuric acid mist was precipitated on the inside wall–electrode, and ozone and the remaining SO_2 were monitored at the exit port. Residence times, humidities, oxygen, and SO_2 concentrations were varied to study the kinetics of the conversion of SO_2 to acid mist. The reaction was zero order with respect to SO_2 in the range tested, and the rate-determining step appeared to be the formation of atomic oxygen by the electrical discharge. Optimum reaction rates occurred at 70% r.h. and above 15% oxygen concentration. Studies of the precipitated droplets indicated a mean size of 6.36 μ before deposition.

Sulfur dioxide mixed with oxygen or air has been oxidized in the presence of an electrical corona discharge by a number of investigators. Miklos et al. (1966) reported efficiencies on the order of 35% for direct oxidation of SO_2 to SO_3 in an airstream. Palumbo and Fraas (1971) concluded that a damped or pulsed high-frequency current was more effective than direct current for SO_2 conversion. In their tests the reactor was placed in an oven at 130°C, and a conversion efficiency of 96% was obtained with a power expenditure of 9 W over a period of 30 min. In the absence of water vapor, only 67% of the SO_2 was converted. Reaction products were identified as elemental sulfur and sulfuric acid. The reaction mechanism was not studied.

Moyes and Smith (1965) presented comparative results for the thermal- and electrical discharge–activation of mixtures of SO_2 and O_2. They showed that the activation by electrical discharge was more efficient, but had doubts about its industrial application for exothermic reactions for which a suitable catalyst was available.

Several questions as to the various reaction mechanisms in such a gas mixture exposed to a corona must be dealt with before launching into pilot scale studies. However, in the case of SO_2, such information is useful especially in certain electrical precipitator operations. The generation of sulfuric acid mist in limited quantities, in power plant stack gases, may have the beneficial side effect of combining with and reducing the resistivity of some types of fly ash, thereby increasing the precipitator's efficiency. Overproduction of the mist, however, would initiate corrosion problems and decrease the overall performance of the precipitator in the long term. Reese and Greco (1968) have shown in tests with TVA precipitators that the presence of H_2SO_4 mist seriously lowered the collection efficiency of electrostatic precipitators. Therefore, it is desirable to have a quantitative estimate of the extent to which various operating conditions in a corona discharge contribute to the conversion of SO_2 to sulfuric acid mist. This paper treats several of the parameters influencing the SO_2 oxidation in a corona to include relative humidity, electrical potential, gas concentrations and flow rates; and reaction mechanisms are proposed, based on results of these studies.

Preliminary tests were made using a small point-to-plane electrostatic precipitator described by Morrow and Mercer (1964). A stream of air at 95% r.h. and 4.0 ppm SO_2 flowed through the electrical field at a rate of 22 l./hr. A potential of -8.0 kV was applied for 120 sec across the 1.0-cm gap. The SO_2 was completely removed from the air. The main phase of this study was directed toward concentrations of SO_2 in the 500–2000 ppm range and much larger volumetric flow rates (1–5 l./min). It was decided to try a wire-to-cylinder type electrical field and to measure SO_2 removed in a dynamic situation at 20°C.

Experimental Arrangement

The experimental apparatus is shown schematically in Figure 1. Regulated compressed air was directed through activated charcoal, and a nitrocellulose membrane filter. The airstream is then split; one branch feeds directly into a glass humidifier column, the other through a flow gage. The two streams are rejoined in a condensate trap–mixing chamber. The mixed airstream flows through a second flow gage and meets the sulfur dioxide. It was possible to inject a constant low-volume flow of SO_2 into the main stream by means of a high-pressure drop capillary coil connected by a tee to the main line. By varying the pressure on the coil from 6 to 22 psig, the SO_2 injection rate could be varied from 2.5 to 25.0 ml/min corresponding to concentrations in the gas stream from 500–5000 ppm.

The dry-bulb temperature of the humidified gas mixture was measured with a total immersion thermometer, and the dew point was monitored with a Cambridge Systems Model 880, Thermoelectric Dew Point Hygrometer. A remote thermistor, connected to the hygrometer, measured the bulk gas temperature of the reactor effluent.

The corona discharge reactor design is similar to a tubular electrostatic precipitator. Details of the construction are shown in Figure 2. The outer grounded electrode is a stainless steel tube, 2-in. i.d. and $^1/_{16}$-in. wall thickness. The tube ends are slotted for O-rings which provide a gas-tight seal with the grooved end plates. The inner, negative electrode is a 32-mil nichrome wire. Direct current was supplied to the wire by a Beckman Model 6205-5MA-M, high-voltage, dc power supply.

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[1] To whom correspondence should be addressed.

[2] Present address, U.S. Army, Rocky Mt. Arsenal, Denver, Colo. 80240.

[3] Present address, Newport Army Depot, P.O. Box 121, Newport, Ind. 47966.

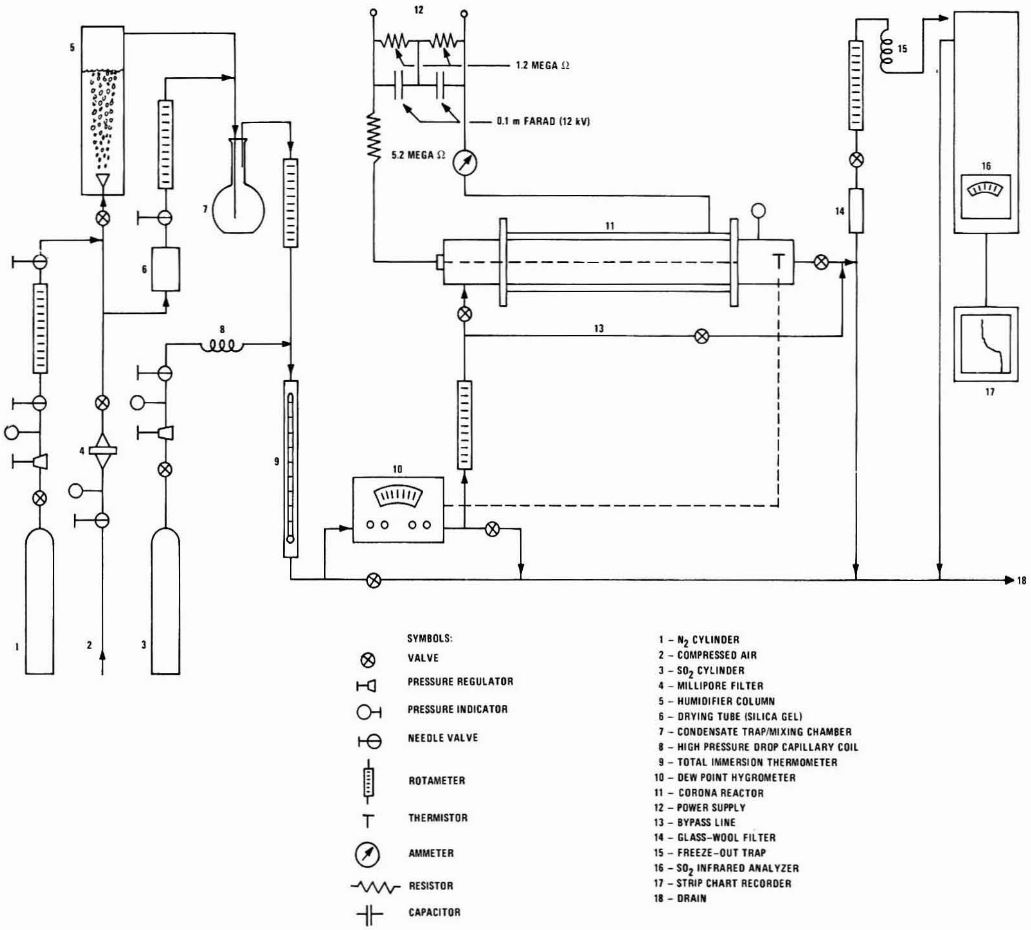

Figure 1. Experimental arrangement

The power unit was continuously variable between 0–25 kV. A 0–1.2 mA ammeter registered the current flow across the wire-cylinder field. A standard threaded electrical connector provided contact between the coaxial wire and the negative terminal of the power supply unit. Auxiliary circuitry was added to reduce the total current flow to less than 1 mA.

The sulfur dioxide concentrations of the gas mixture were monitored with a Beckman Model 215A Infrared Analyzer. About 100 ml /min of reactor effluent was diverted through a helical glass coil immersed in an ice–acetone bath to remove moisture from the sample stream, and then a guard filter before entry into the analyzer. A continuous readout of the SO_2 concentration was recorded on a strip chart. The error in the SO_2 determination was on the order of $\pm 5.0\%$. Dry air produced an ir scale deflection equivalent to 25–50 ppm SO_2. Additional errors due to the presence of water vapor in the sample stream were eliminated by the cold trap.

Ozone generated in the reactor was determined using a modified ASTM Procedure D1609-60 (1964). A portion of the reactor effluent was bubbled through 100–200 ml of alkaline KI absorbing solution and the absorbance of the solution was measured at 352 μ with a Beckman DU Spectrophotometer.

Operating Procedure

A kinetic study of the corona–sulfur dioxide reaction was conducted by measuring the loss in SO_2 during a given residence period of the gas mixture flowing through the reactor. The initial SO_2 concentration could be held at a fixed value while the gas stream volume was varied, thus varying the residence time. Also the SO_2 concentration could be varied for a fixed volumetric flow rate.

The relative humidity of the mixed gas stream was controlled by adjusting the ratio of dry to saturated airstream flow rates. When initial SO_2 concentration, air humidity, flow rate, and temperature reached the desired constant values (1.5–2 hr), the power was applied and the concentration of SO_2, as recorded by the ir, was observed to drop until it reached a lower constant value. Approximately 5 min elapsed before steady-state reaction conditions were attained in the reactor and registered by the ir. The power supply voltage, corona current, and the SO_2 concentration were continuously recorded. After the SO_2 concentration reached a lower stable value, the power supply was cut off and the system allowed to return to nonreaction conditions to ensure that the initial SO_2

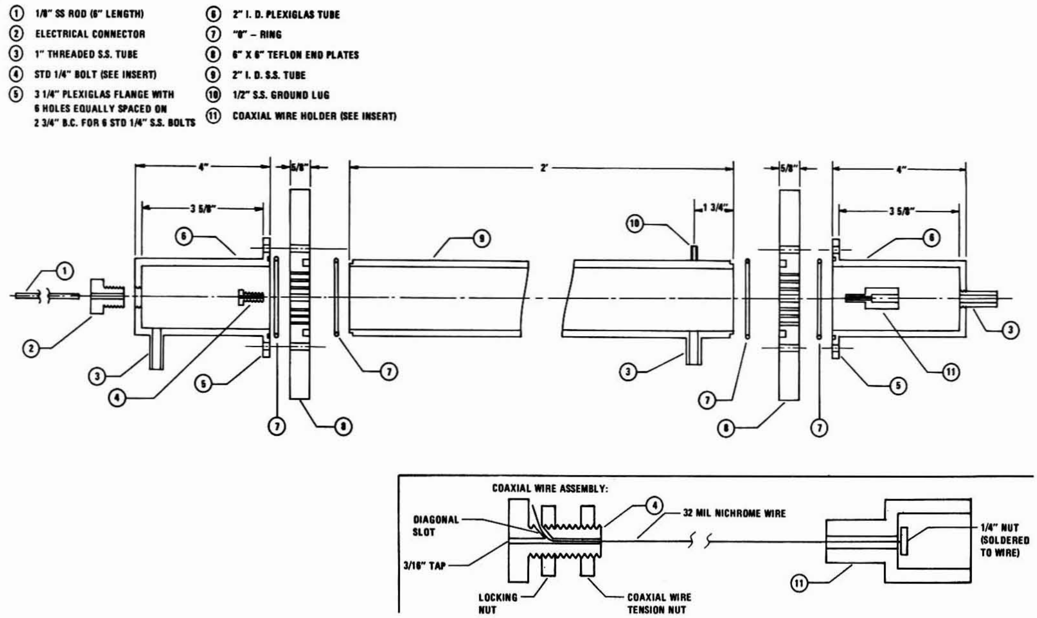

Figure 2. Corona discharge reactor

concentration had not changed. The system was sensitive to leaks in the gas-conveying apparatus, and seals had to be checked before each run.

The infrared analyzer was calibrated before each experiment over the ranges 0–1000 ppm and 0–5000 ppm SO_2. Dry nitrogen was used as a zero gas, and calibrated gas mixture (Matheson) of 5162 ppm SO_2 in N_2 provided the span gas.

ASTM Procedure D-1609-70 had to be modified to measure the relatively high O_3 concentrations produced in the reactor. The ozone generation was determined first in a series of blank runs with only humidified air flowing through the energized reaction zone. The gas flow rate was varied from 0.5 to 5.0 l./min, and the relative humidity was maintained constant at about 70%. The reactor effluent was bubbled through a coarse gas dispersion tube immersed in 100–200 ml of alkaline KI solution. It was necessary to dilute the absorbant solution by as much as tenfold before continuing with the ASTM procedure. Also, it was necessary to use 30 wt % H_2O_2 rather than the standard 3% to obtain stabilized absorbance readings. The instability problem was thought to be a result of the presence of interfering oxides of nitrogen generated in the reactor and picked up in the absorbing solution. Ozone measurements were also made in the presence of SO_2.

Sulfuric acid mist was formed in the reactor by the hydration and nucleation of sulfur trioxide in the humid airstream. The mist was deposited on the inside grounded wall of the cylinder owing to the action of the electric field. The size of the deposited droplets was determined according to the method of Horstman and Wagman (1967). Glass microscope slides (0.7 × 7.62 cm) were coated with a thin film of reagent grade iron in a Kinney vacuum evaporator. The iron film thickness was on the order of 0.5 μ. The metal-coated slides were then placed lengthwise along the wall of the reactor. Acid droplets deposited on the metal film left an etched replica, which could be viewed by light or electron microscopy. Photographs were made and size analysis performed with a Zeiss TGZ-3 Particle Size Analyzer. The acid content of the reactor residue was determined by disassembling the reactor after a test and washing with 400–500 ml of deionized water. The acid concentration of the wash was then measured with a pH meter and checked by titration with a standardized NaOH solution, using Bromothymol Blue as an indicator.

Results

Reaction Kinetics. The rate of dissappearance of SO_2 appeared to be zero order with respect to SO_2 for those initial concentrations investigated. Figure 3 shows initial reaction rates for SO_2 concentrations between 500 and 3000 ppm. The rate of SO_2 removal appeared to reach a steady-state value after the first 1.5 min. These tests were made with air at 70% r.h.

We decided to test at the 70% level after a series of experiments at various humidities (Figure 4) showed that the removal rate was an optimum for that particular water vapor content. At higher humidities, the dielectric properties of the gas were probably altered, and corona breakdown and sparkover frequently occurred. During a test at 70% r.h. the temperature of the reactor effluent increased by 6.3°C for the 2.5 min residence time. This was a result of the dielectric heating by the electric discharge and the exothermic nature of the chemical reaction. The humidities reported are therefore inlet values. The variation in initial humidity values was ±2.0%.

The effect of oxygen concentration on reaction rate was quite significant below 15% for an initial SO_2 concentration of 1000 ppm (Figure 5). In these tests the gas flow rate was held constant at 5.0 l./min and the O_2 concentration varied from 0–21% by diluting the primary airstream with nitrogen. Sulfur dioxide was not removed when oxygen was absent from the gas mixture. At oxygen concentrations above 15%, the SO_2 removal rate appeared to be constant.

The kinetics of O_3 formation in the corona discharge reactor was investigated in the presence and absence of SO_2. All tests

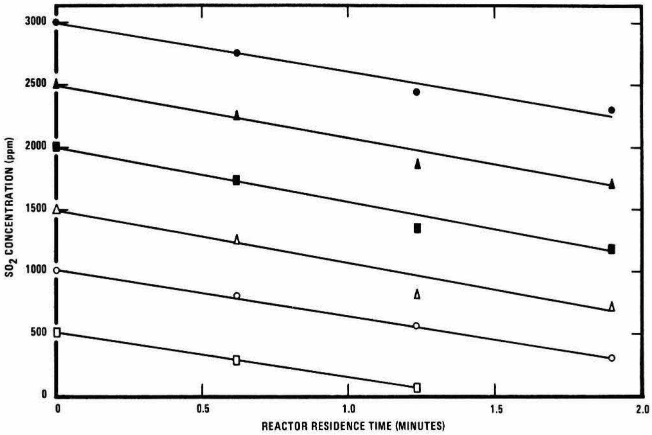

Figure 3. Initial removal rates for various SO_2 concentrations

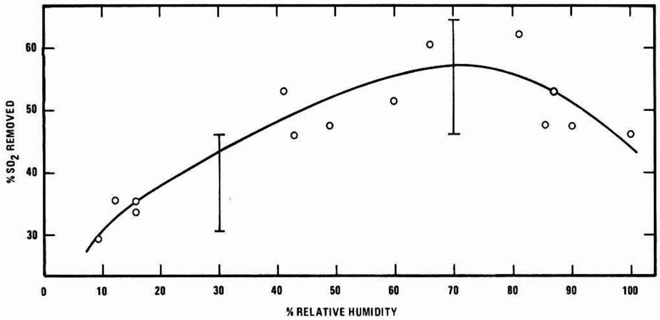

Figure 4. Fraction of sulfur dioxide removed as a function of relative humidity of the carrier airstream

Vertical lines represent spread in data; 1.0 l./min flow rate at 1000 ppm SO_2 initial concn

were conducted with air at 70% r.h. These data are presented in Figure 6. In comparing those tests where 1000 ppm SO_2 was present with tests which included no SO_2, one can see that practically all of the ozone generated by the discharge is absent in the SO_2 oxidation reaction. The error in the O_3 determination is approximately ±10% for the flow rates discussed. This was due mainly to variations in the corona discharge characteristics at the 70% r.h. of the airstream.

Power Utilization. A series of experiments was conducted to determine the specific energy consumption as a function of flow rate, SO_2 removed, and applied power. The effects on power consumption of wall loading as a result of the precipitation of acid droplets was also investigated. Figure 7 shows the effect of various power levels on the SO_2 exit concentration for three flow rates. The SO_2 concentration drops off rapidly with corona onset, and the curves indicate that application of sufficient power would result in essentially complete removal of SO_2. For the 0.5 l./min flow rate, the extrapolated value of 15 W represents total SO_2 removal. This is equivalent to 0.015 kW-hr/SCF (15 kW-hr/1000 ft^3) or about one sixth the power requirement obtained by Browne and Stone (1965) with a cylindrical quartz reactor.

In an effort to determine the rate at which power consumption varies during reactor operation, the discharge was operated continuously for 240 min. The power required to remove 87.5% SO_2 from a stream flowing at 0.5 l./min at 1000 ppm initial SO_2 concentration increased by about 20% in the first 100 min and then stabilized at 0.0134 kW-hr/SCF (Figure 8). Decreases in reactor efficiency were much more noticeable if a surface film was allowed to form on the inside wall of the reactor between runs. In two experiments, we compared the results of untreated reactor walls with a second run wherein the walls were etched with concentrated hydrochloric acid prior to the test. In both cases a gas flow of 1 l./min at 70% r.h. and 1000 ppm SO_2 was exposed to the corona for 30.0 min. The power consumption dropped from 0.0055 to 0.0050 kW-hr/SCF in going to the etched tube. In addition, the fraction of SO_2 recovered increased from 32.5 to 50% on a steady-state basis. Therefore all tests were repeated, and the results reported here reflect the SO_2 removal rates for the reactor which had been thoroughly cleaned prior to each reaction.

Acid Mist. Sulfuric acid mist formed in the reactor by the hydration of SO_3 and deposited on the reactor wall by the electrostatic field was sampled for particle size analysis. A total of 3215 particles were counted and sized from 32 photographs over eight segments of microscopic slides. The photos were taken at a total magnification and enlargement of 239×. The etched imprints were sized, and this data was used to estimate the original droplet diameter. The size distribution for the deposited droplets displayed a log-normal probability pattern

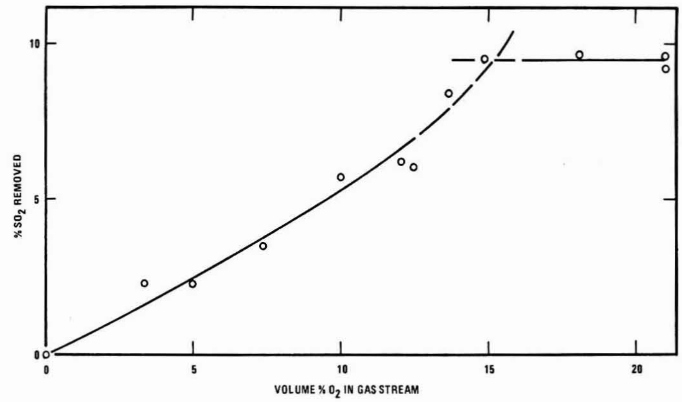

Figure 5. Influence of oxygen concentration on sulfur dioxide removal, 5.0 l./min gas flow rate at 1000 ppm SO_2 initial concn

as shown in Figure 9. The geometric mean diameter, D_{gc}, was 23.1 μ, and the standard deviation, σ_{gc}, was 2.18. The size of the impacted droplet was essentially random with respect to where the samples were taken in the tube; there was no correlation of size with distance down the tube. It appeared then that nucleation occurred along the entire length of the reactor, and that the particles did not travel far, in the axial direction before being deposited on the wall. Knowing the time elapsed during the deposition of the counted particles, and the area over which these particles fell, the particle deposition rate PDR, could be calculated. This amounted to 10^4 particles/cm^2 min or 0.8×10^6 particles/min for the whole tube. Assuming that the SO_2 removal rate is equivalent to the H_2SO_4 production rate, $W_{H_2SO_4}$, and that all of the acid formed becomes acid nuclei, a loss of 555 ppm SO_2 in a 1-l./min stream would produce 1.32×10^{-3} cm^2 H_2SO_4/min. Therefore, the theoretical volume of the mean-sized droplet before impaction is

$$V_{\text{drop}} = \frac{W_{H_2SO_4}}{PDR} = 1.35 \times 10^{-10} \frac{\text{cm}^3}{\text{particle}} \qquad (1)$$

This is equivalent to an average diameter of 6.36 μ.

In five separate tests we compared the SO_2 disappearance as measured by the ir, with the H_2SO_4 formed in the reactor and cold trap, as measured by titrimetric techniques. The results showed that about 75% of the SO_2 removed was present in the form of H_2SO_4. This may have been a result of reduction of the hydrogen ion to H_2 gas in the reactor, before the titrimetric measurements were made. More than 99% of the acid formed was collected in the reactor; the remainder being trapped in a downstream glass wool filter and cold trap.

Other Tests. In two tests, we examined the effect of NO_x on SO_2 conversion. The reactor was first operated with no NO_x; in the second test we added 50 ppm NO, and in the third 50 ppm NO_2. In the latter two cases there was no observable difference in the amount of SO_2 removed. Finally, we insulated all but 1 in. of the nichrome wire at the entrance with a teflon sleeve. The SO_2 conversion was decreased by 90%, indicating that the activation process occurs all along the wire cathode.

Discussion

Since the rate of disappearance of SO_2 as H_2SO_4 appeared to coincide with the formation of ozone (Figure 6), it seemed that the rate-determining step in the oxidation of SO_2 was the ozone generation step. Figure 10 is a plot of

$$\frac{\Delta SO_2}{(SO_2)_0} \text{ vs. } \frac{O_3}{(SO_2)_0}$$

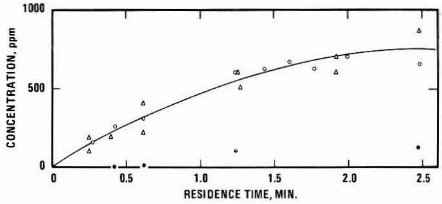

Figure 6. Ozone generation rates

Without SO_2, ○; with 1000 ppm SO_2 ●; SO_2 removal rate △, for 1000 ppm initial concentration

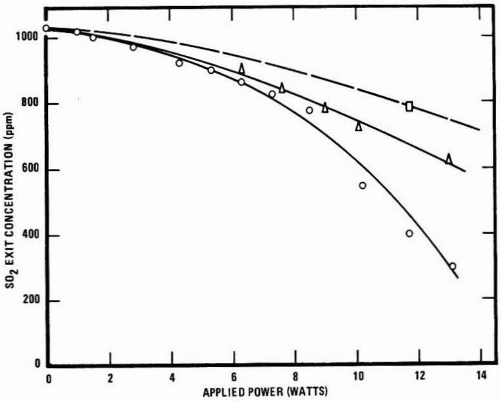

Figure 7. Effect of applied power on SO_2 removal for various flow rates

0.5 l./min, ○; 1.0 l./min △; 3.0 l./min □; initial SO_2 concn, 1000 ppm and 70% r.h.

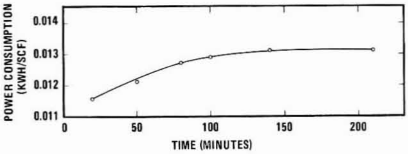

Figure 8. Power consumption per SCF vs. operation time

Flow rate, 0.5 l./min, 1000 ppm SO_2, 70% r.h.

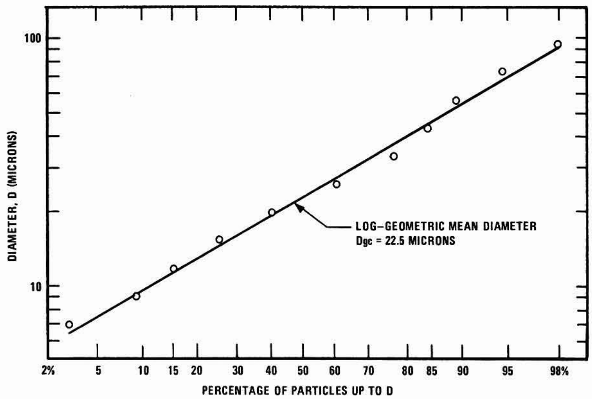

Figure 9. Cumulative particle-size distribution for acid droplets impacted on reactor wall

for various initial $(SO_2)_0$ values and residence times. The O_3 values were taken from Figure 6 for the ΔSO_2 values corresponding to the same residence times. It is evident that there is very nearly a stoichiometric ratio of moles of sulfur dioxide removed for every mole of ozone produced.

Filippov and Emel'yanov (1961) and Filippov and Vendillo (1961) conducted an extensive kinetic study of the electrical synthesis of ozone under flow conditions, and proposed the following expression for O_3 synthesis:

$$\frac{d[O_3]}{dt} = k_1[O_2] - k_2[O_3] \tag{2}$$

The ordinary laws of kinetics may be applied to the case of flow reactions in electrical discharges by replacing the independent time variable in Equation 2 by a kinetic power factor U/v, where U is the applied power, watts, and v is the linear velocity, cm/sec. Therefore, Equation 2 may be solved for the case of excess O_2:

$$[O_3] = \frac{k_1[O_2]}{k_2}\{1 - \exp(-k_2U/v)\} \tag{3}$$

The above equation was fitted to the data presented in Figure 6 with the result that our data was represented quite well by such an expression with

$$k_1O_2 = 11.55 \text{ ppm sec}^{-1} = 52.1 \text{ ppm cm (Wsec)}^{-1}$$
$$k_2 = 0.0154 \text{ sec}^{-1} = 0.0695 \text{ cm (Wsec)}^{-1}$$

We considered several possibilities for the mechanism of SO_2 removal. Gerhard and Johnstone (1955) investigated the photochemical oxidation of SO_2 by sunlight. They found a first-order relationship

$$\frac{d[SO_2]}{dt} = -k_3[SO_2] \tag{4}$$

where $k_3 = 1.6 \times 10^{-6}$ sec^{-1}. This rate is about 10^4 slower than what we experienced with the corona discharge reactor. Also there seems to be no means of accounting for the loss of ozone on this route.

Powers and Cadle (1965) tested the reaction

$$SO_2 + O_3 \xrightarrow{k_4} SO_3 + O_2 \tag{5}$$

with concentrations 1–10% SO_2, 1% O_3, and 1% water vapor and found that less than 0.1% of the SO_2 had reacted in a 24-hr period. This work was confirmed by Dunham (1960) who found no significant condensation nuclei of H_2SO_4 from the SO_2–O_3 reaction. Mulcahy et al. (1967) studied the kinetics of reactions between atomic oxygen and sulfur dioxide. Their work showed that the kinetics of the SO_2 conversion can be explained by the termolecular combination reaction:

$$O + SO_2 + O_2 \xrightarrow{k_5} SO_3 + O_2 \tag{6}$$

where

$$k_5 = 5.4 \times 10^{-6} \text{ (ppm)}^2 \text{ sec}^{-1}$$

If we take $[O] \approx [O_3]$, then at equilibrium

$$[O] \approx [O_3] = \frac{k_1[O_2]}{k_2} \tag{7}$$

so an estimate can be made of the rate of formation of SO_3:

$$\frac{d[SO_3]}{dt} = k_5[SO_2][O_2]\frac{k_1[O_2]}{k_2} \tag{8}$$

and this can be compared with the maximum rate of formation of O_3

$$\left(\frac{d[O_3]}{dt}\right)_{\max} = k_1[O_2] \tag{9}$$

$$\frac{\dfrac{d[SO_3]}{dt}}{\left(\dfrac{d[O_3]}{dt}\right)_{\max}} = \frac{k_5[SO_2][O_2]}{k_2} \tag{10}$$

$$= 7.4 \times 10^4 \gg 1$$

Therefore even though the $[O_2]/[SO_2]$ relative concentration is on the order of 20/1, the relatively high rate constant in Equation 6 favors the formation of SO_3 and the O_3 will be formed in negligible amounts.

Injection of oxides of nitrogen showed no effect on reaction rates; however, the concentrations used (50 ppm) may have been inappropriate. Wilson et al. (1970) observed that SO_2 is removed by a product of the reaction of NO_2 and O_3. They suggested that NO_3 or N_2O_5 reacts with SO_2 to form SO_3 and NO_2. Gerhard and Johnstone (1955) reacted 1 to 2 ppm of NO_2 with 10 to 20 ppm SO_2 in irradiated light (2950–2650Å) and found no measurable effect. However, Renzetti and Doyle's experiments (1960) showed that the addition of 1 ppm NO_2 to 0.14 ppm SO_2 enhanced the photooxidation of SO_2. Further experiments at higher NO_2 concentrations will reveal whether this enhancement effect can be duplicated in the case of corona discharge–stimulated reactions.

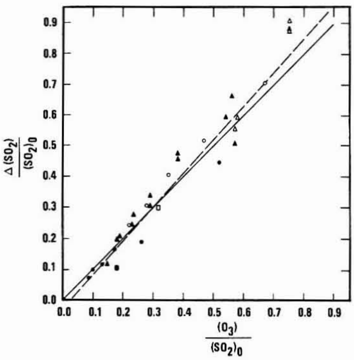

Figure 10. Fraction of sulfur dioxide removed vs. moles of ozone generated during the same residence time

Solid line represents $\Delta(SO_2) = (O_3)$; dashed line is least-squares fit. Residence times = 2.5 min, △; 1.92 min, ○; 1.25 min, ▲; 0.63 min, □; 0.42 min, ●; 0.32 min, ■

The nucleation process was not studied in this work, but since air humidified by a bubbling process contains water nuclei and since the metal wire cathode is continuously ejecting metal particles, the presence of condensation nuclei may enhance the overall rate of droplet formation and ultimate size of the deposited droplets. This is not expected to be a rate-limiting step, however, since SO_3 is strongly self-nucleating in the presence of water vapor, and proceeds at rates far greater than the SO_2 oxidation step.

Conclusions

The rate of oxidation of sulfur dioxide in humid air in the presence of a corona discharge is zero order with respect to SO_2 in the range 500–3000 ppm. The reaction was strongly dependent on oxygen and the oxidation rate diminished for O_2 concentrations below 14%. By measuring the rate of ozone formation in the absence and presence of SO_2, it appears that the rate-controlling mechanism for the SO_2 oxidation lies in the breakdown of the oxygen molecule by the corona discharge to form atomic oxygen. Apparently the SO_2–O reaction is several orders of magnitude faster than the O_2–O reaction. About 75% of the SO_2 removed precipitated in the form of sulfuric acid mist on the wall of the reactor. Studies of the precipitated droplets indicate a mean size of 6.36 μ before deposition. Deposition patterns were consistent for the entire length of the reactor suggesting that aerosol movement was almost exclusively in the radial direction. Oxides of nitrogen at 50 ppm showed no measurable effect on the sulfur dioxide reaction rate.

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Mercury Levels in Muscle Tissues of Preserved Museum Fish

Ronald J. Evans and Jack D. Bails
Fish Division, Michigan Department of Natural Resources, Lansing, Mich. 48926

Frank M. D'Itri[1]
Institute of Water Research and Department of Fisheries and Wildlife, Michigan State University, East Lansing, Mich. 48823

The recent discovery of mercury contamination in the fish populations of the Lake St. Clair–Western Lake Erie area of the Great Lakes has caused some speculation as to the prior duration and extent of this contamination. Knowledge of this aspect of the present mercury pollution problem in this area would give some insight into the length of time that a human health hazard has existed. It would also help demonstrate whether changes in the mercury content of the fish could be correlated with increases in the industrialization and urbanization of the Detroit area.

Until recently, the main source of mercury into the environment has been the erosion and leaching of mercury-containing geological formations by rainfall that also transports the mercury to streams and lakes by groundwater runoff. Since the industrial revolution, however, increasing

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[1] To whom correspondence should be addressed.

■ Flameless atomic absorption spectrophotometry was used to establish the total mercury levels in 57 preserved fish specimens of various species collected in the Lake St. Clair–Western Lake Erie region of the Great Lakes between the years of 1920–65. Only five fish were found to contain mercury levels in excess of 0.5 ppm—three large muskellunge collected in Lake St. Clair in 1939 (2.38, 1.57, and 1.58 ppm) and two adult sea lampreys collected in the Clinton River tributary to Lake St. Clair in 1938 (0.90 and 1.29 ppm). A trend was established relating the mercury content of selected categories of fishes with the year and location of collection for the fish specimens. The 1970–71 mercury levels in fish from the two study areas were found to average more than those preserved museum specimens in the same categories taken from the same area.

amounts of mercury have been lost to the environment from waste products as a result of manufacturing processes that utilize mercury or from the disposal of industrial and consumer products which contain mercury compounds (D'Itri, 1972).

In urban and industrial areas, the sanitary sewer systems serve as a convenient disposal system for mercury-containing consumer products. On the average, the mercury concentration of sewage treatment plant effluents are one order of magnitude greater than the water course that receives it (D'Itri, 1972). Klein and Goldberg (1970) have reported that the mercury concentration in surface sediment samples near municipal sewer ocean outfalls are eight to 10 times higher than similar sediments that are farther from the outfall.

Large quantities of mercury are lost to the environment through burning or other utilization of fossil fuels. The very limited data available in the literature indicates that while levels of mercury in coal are highly variable, concentrations in the range of 0.1 to 1 ppm are common (Joensuu, 1971). Therefore, considering a yearly worldwide consumption of approximately 3 billion tons of coal (Young and Gallagher, 1968), 0.6 to 6 million lb of mercury are lost to the environment from this source alone.

Another potentially very large environmental mercury contamination source occurs in the recovery or use of raw materials which contain small amounts of mercury. Klein (1971) has identified the smelting of sulfide ores of various metals as a major source of mercury to the atmosphere and has estimated the yearly worldwide contribution from this source to be between 6 and 40 million lb.

The accumulative effects of all sources of mercury in the Great Lakes area in the past 70 years has been great. For example, using known rates of sediment accumulation, Thomas (1972) found that the levels of mercury in the lake sediments began to rise above background levels of 358 ppb about the year 1900. Between 1900 and 1940, a gradual increase in mercury levels was noted until the period between 1940 and 1952 when the levels quadrupled over the mean background level. Since 1950, the mercury levels in the sediments have fluctuated, but they have shown a steady, slow increase to the present time.

In Sweden, Berg et al. (1966) analyzed the mercury content of feathers on birds preserved in several Scandinavian university museums. They were able to correlate a sharp increase in the mercury content of the feathers of seed-eating birds with the introduction of alkylmercury fungicides as grain seed treatments in the early 1940's. Moreover, they also demonstrated a slow but significant increase in the amount of mercury found in the feathers of fish-eating birds, beginning around 1900. They speculated that this increase in the mercury levels of fish-eating birds paralleled Sweden's industrial growth and was the result of the attendant increased losses of mercury in the environment.

In this study, attempts were made to test this general method of utilizing preserved museum samples to provide information about historical mercury levels in fish from the study area. To accomplish this, muscle tissue samples were taken from preserved fish specimens originally collected in the St. Clair and Detroit Rivers and Lake St. Clair as well as the western basin of Lake Erie (Figure 1), and includes the area most seriously affected by mercury contamination in the United States.

Methods and Materials

Preserved fish specimens that were originally collected from these waters were obtained primarily from the fish collection at the University of Michigan Museum of Zoology. Additional preserved fish were supplied by the Department of Biology at Wayne State University and the Department of Fisheries and Wildlife at Michigan State University.

The tissue sample from each preserved fish specimen was taken from the dorsal muscle, located between the head and dorsal fin. After removing the skin, approximately 2 grams of this preserved muscle tissue were gently pressed between absorbent (mercury-free) tissue paper to remove as much of the preservant solution as possible. This sample was then homogenized with 15 ml of distilled water for two min in a

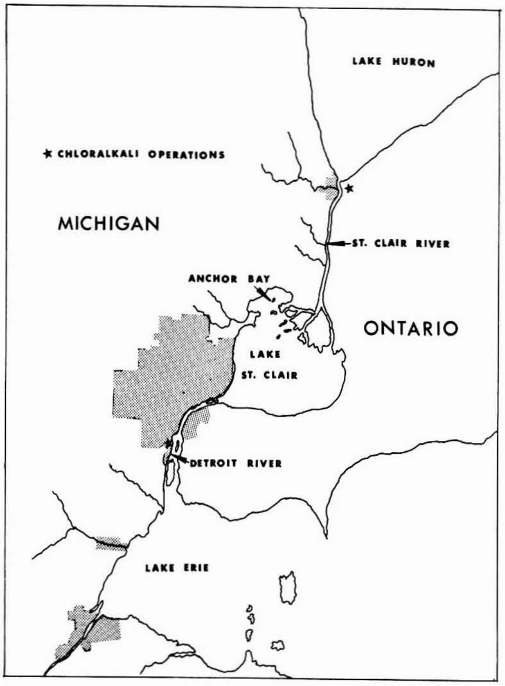

Figure. 1. Region of the Great Lakes where the preserved museum fish were originally taken

Waring Blendor equipped with a mini-container attachment. The dry weight of fish per unit volume of this slurry was determined by drying a 3-ml portion of the homogenate to a constant weight in a vacuum oven at 50°C with 250 mm pressure for 25 hr. This dried material was then discarded.

For the mercury analysis, 3 ml of the homogenated preserved flesh was pipetted into a 100-ml volumetric flask. Then 5 ml of concentrated sulfuric acid was added and the sample heated in an 80°C waterbath for 15–30 min to decompose the homogenate. The flask was cooled in an ice bath before 15 ml of a 6% w/v potassium permanganate was added to it after which the solution was removed from the ice bath. After the solution reached room temperature it was returned to the 80°C water bath for from 15 to 20 min or until the frothing action ceased. Then it was transferred to a hot plate and heated to its incipient boiling point. After the solution had cooled to room temperature, enough 10% w/v hydroxylamine hydrochloride solution was added to eliminate the excess potassium permanganate and manganese dioxide. Then the solution was made up with distilled water to the calibration mark. The measurement of the total mercury of each sample has been described (Annett et al., 1972).

Since storage in formalin, and especially storage in alcohol. causes shrinkage and dehydration of the flesh of the fish, a 75% value for the percentage of water in fish muscle was assumed, and the dry weight mercury concentrations were divided by a factor of 4 to arrive at the live weight mercury concentrations.

Results and Discussion

Preserved flesh samples were obtained from all museum fish samples available to the authors from the study area without regard to species, sizes, collection dates or the specific locations from which the fish were originally taken. The result is a collection of muscle tissue samples taken from 57 individual fish of 26 different species in the study area between 1920 and 1965. The fish varied between 10 and 102 cm in length and between 1 and 8 years in estimated age.

The museum specimens were originally collected throughout the study area with: 4 fish from the St. Clair River, 24 from Lake St. Clair, 11 from the Detroit River, and 18 from western Lake Erie. Breaking down the collection data into decades: 9 fish were collected from 1920–29, 20 from the 1930's, 7 from the 1940's, 12 from the 1950's, and 9 from 1960–65. Duplicate analyses were accomplished on all specimens whenever the size of the fish sample was sufficient, and additional analyses for a given sample were also performed if the original duplicate analyses did not agree well. The complete results of the total mercury analyses of the preserved fish flesh are available from the American Chemical Society Primary Publications Microfilm Depository Service. A summary of these data show the following range of averages after duplicate tests:

27 fish with mercury levels between 0.01 and 0.09 ppm
13 fish with mercury levels between 0.10 and 0.19 ppm
6 fish with mercury levels between 0.20 and 0.29 ppm
6 fish with mercury levels between 0.30 and 0.41 ppm
5 fish with mercury levels between 0.90 and 2.38 ppm

These data show that 70% of the preserved fish contained total mercury levels of less than 0.20 ppm or about the same mercury levels reported in some freshwater fish in 1934, vis 0.03–0.18 ppm (Stock and Cucuel, 1934). Moreover, Great Lakes fish which are currently taken from uncontaminated areas generally show total mercury levels below 0.20 ppm. The data also show only five preserved fish specimens with mercury levels in excess of the United States Food and Drug Administration interim action level of 0.5 ppm. These fish were three muskellunge taken in the Anchor Bay area of Lake St. Clair in 1939 and two adult migrating sea lampreys collected in 1938 from the Clinton River which empties into Anchor Bay. Significantly these species are also the highest-level predators in the waters surveyed and the muskellunge at 40+ in., 20+ lb, and approximately 7–8 years in age, clearly the largest and oldest fish in the survey.

It is apparent from mercury analyses reported for fish throughout the country that the mercury concentration rates vary between species. Generally, the highest trophic level species like muskellunge and sea lamprey have the highest levels of mercury while the planktivores like smelt and gizzard shad show the lowest levels. During 1970, extensive fish samples were collected from Lake St. Clair by the Michigan Department of Natural Resources. These fish samples were analyzed by various laboratories. The Lake St. Clair fish species collected were placed in four categories given in Table I according to the mean level of mercury found in their muscle tissues (Bails, 1972). Sea lamprey were not sampled from Lake St. Clair during 1970; however, fresh sea lamprey that were obtained and analyzed by the authors from Lake Superior indicated that the mercury content of the predatory sea lamprey averaged three to four times greater than the primary prey species, thereby placing the sea lamprey in Category I.

Figure 2 graphically compares the mean mercury levels by category of preserved fish specimens from Lake St. Clair and the St. Clair River to those obtained during the 1970 sampling from the same area. The specimens collected before 1945 show the same low mean levels for all categories except one. Sea lamprey and muskellunge, as mentioned earlier, showed high levels even prior to 1945. The 1965 samples indicate that all specimens except those in Category IV had

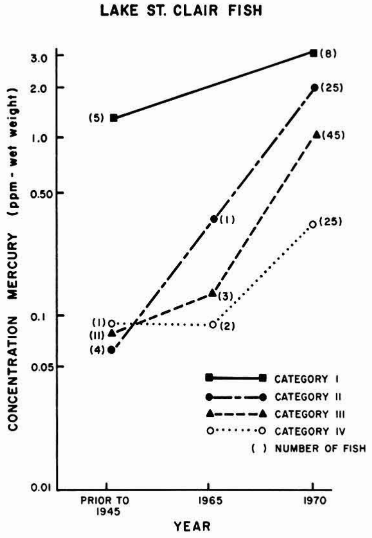

Figure 2. Comparison of mean mercury levels of preserved museum fish specimens from Lake St. Clair and the St. Clair River to mean mercury levels of fresh fish taken in 1970 from the same area

Table I. Scientific Names and 1970 Mean Mercury Levels of Fish Taken From Lake St. Clair and the St. Clair River

Common name	Scientific name	Category	1970 Mean mercury levels, ppm
Muskellunge	*Esox masquinongy*	I	>3.0
Sea lamprey[a]	*Petromyzon marinus*		
Lake sturgeon	*Acipenser fulvescens*	II	2.0–3.0
Northern pike	*Esox lucius*		
Sauger	*Stizostedion canadense*		
Smallmouth bass	*Micropterus dolomieui*		
Walleye	*Stizostedion vitreum*		
White crappie	*Pomoxis annularis*		
Channel catfish	*Ictalurus punctatus*	III	0.5–2.0
Drum (freshwater)	*Aplodinotus grunniens*		
Longnose gar	*Lepisosteus osseus*		
Rock bass	*Ambloplites rupestris*		
White bass	*Morone chrysops*		
Yellow perch	*Perca flavescens*		
Black bullhead	*Ictalurus melas*	IV	<0.5
Bluegill	*Lepomis macrochirus*		
Carp	*Cyprinus carpio*		
Quillback	*Carpiodes cyprinus*		
Gizzard shad	*Dorosoma cepedianun*		
Goldfish	*Carassius auratus*		
Bigmouth buffalo	*Ictiobus cyprinellus*		
Silver redhorse	*Moxostoma anisurum*		
Rainbow smelt	*Osmerus mordax*		
Yellow bullhead	*Ictalurus natalis*		

[a] Not taken from study area, see text for explanation.

elevated mercury levels. It is interesting to note that by 1965 the various concentration rates began to separate species by mercury levels. The 1970 Lake St. Clair and St. Clair River data represents a combined total of over 100 analyses of fish representing each of the four categories.

The sampling of western basin Lake Erie and Detroit River fish during 1970 and 1971 indicated that mercury levels were approximately half those found for the same species in Lake St. Clair and the St. Clair River. This categorization of species with respect to 1970 mercury content applied equally well to fish taken from Lake Erie and the Detroit River. Unfortunately, no sea lamprey or muskellunge were taken from the western basin of Lake Erie or the Detroit River during 1970 or 1971, and Category IV is not represented. However, the other three categories were well represented by a number of species during 1970–71. In Category II, the western basin Lake Erie and lower Detroit River samples averaged between 1.0 and 2.0 ppm mercury; the Category III fish samples averaged between 0.3 and 1.0 ppm; and Category IV fish averaged less than 0.3 ppm.

Figure 3 compares the 1970–71 mercury levels in fish from the western basin of Lake Erie and lower Detroit River to mercury levels in the preserved specimens taken prior to 1937 and during the interval from 1942–64. The trends are the same as observed in Lake St. Clair. Prior to 1937, fish in categories II, III, and IV had mean mercury levels 0.2 ppm or less. The one muskellunge taken in 1922, representing Category I, had a mercury level of 0.37 ppm. In the 1942–64 period, the mercury levels increased slightly in the three categories of fish analyzed from this time interval. By 1970, the mercury levels in fish had risen to the point where only Category IV species had mercury levels less than 0.3 ppm.

It is difficult to postulate a definite reason for the high mercury concentrations in the lampreys and muskellunge captured in the Anchor Bay region of Lake St. Clair. The high levels could possibly be due to mercury pollution of the bay or lake prior to 1939 since mercury levels in excess of 0.5 ppm would be an indication of a nearby source of mercury pollution. A mercury pollution source outside of the Anchor Bay region must also be considered since both lampreys and the muskellunge are highly mobile fish.

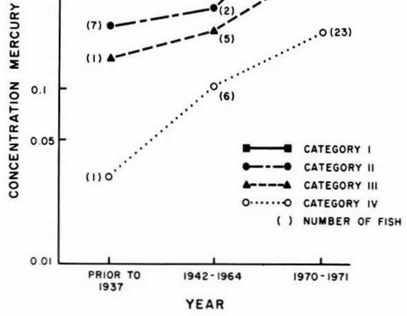

Figure 3. Comparison of mean mercury levels of preserved museum fish specimens from the Detroit River and Lake Erie to mean mercury levels of fresh fish taken in 1970 from the same area

The increases in mercury levels in fish over the last 50 years, indicated in Figures 2 and 3, appear to confirm previous research in Sweden which recorded increased mercury contamination of the environment with increases in industrialization (Johnels et al., 1967). Generally, the chloralkali manufacturing operation utilizing continuous mercury cathode cells at Wyandotte, Mich., and Sarnia, Ont., are considered the largest single contributors to mercury pollution in this area of the Great Lakes. However, since these chloralkali operations did not begin until 1939 and 1947, respectively, they can be eliminated as the source of the mercury found in these fish before 1939. Nevertheless, the dramatic increase in mercury levels between 1964 and 1970 in the St. Clair River, Lake St. Clair, Detroit River, and western basin Lake Erie complex may be related to the substantial increases in the losses of mercury from chloralkali plants reported by Fimreite (1970) and Branch (1970) during the late 1960's.

Ideally, for a survey of this type to yield the maximum usable data, the preserved fish specimens should all be of comparable groups of species, size, and age as well as being collected at the same sampling locations at selected time intervals throughout the survey. Also, the preserved fish specimens should include the large aggressive predatory species which have been shown to be active biological concentrators of methyl mercury in the study area. Furthermore, statistical validity considerations demand that a minimum of three fish of the same species, size, and age be analyzed from each of the four principal waterways of the study area. However, because of the difficulty in obtaining preserved fish specimens, it is recognized that this survey falls short of ideal conditions. Nevertheless, categorizing the fish into distinct groups did generate five separate curves (Figures 2 and 3) which illustrate the same trends. Mercury levels in fish from Lake St. Clair and Lake Erie have been increasing since the early 1940's and the rate of increase accelerated in the late 1960's. It is unlikely that the close correlation between these five curves is due to chance alone.

If these curves do accurately reflect mercury levels in fish from the study area over the past decade, the human health problems associated with mercury levels in fish are relatively recent. The majority of fish taken by fishermen prior to 1966 probably had mercury levels below 0.5 ppm, the current Food and Drug Administration action level.

Acknowledgment

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Separation of Oil Dispersions from Water by Fibrous Bed Coalescence

William M. Langdon, Prakash P. Naik, and Darsh T. Wasan[1]

Department of Chemical Engineering, Illinois Institute of Technology, Chicago, Ill. 60616

Recently, the treatment of oily effluents in inland waterways and coastal waters has become an urgent problem. Aqueous effluents from many industries—chemical, petroleum, and metallurgical—often contain oily material. These oily materials may be present as a film on the water surface or in the form of a dispersion with water. They may have some of the soluble substances extracted by water, and finally form semisolid deposits of oil and sediment.

A very general problem of particular importance is the separation of oil dispersions which are formed in high-speed turbine and centrifugal pumps. An initial or primary separation of massive amounts of oil can be achieved effectively by gravity settling. This is not effective for secondary dispersions (mean droplet size of 10 μ and lower) which constitute a relatively small volume fraction of oil (usually 1000 ppm and lower). The Stokes settling velocity for such droplets is very small and thus require prohibitively long separator residence times for separation of two phases by gravity. Various auxiliary procedures have been used to promote rapid coalescence

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[1] To whom correspondence should be addressed.

■ A 1-ft^2 coalescer unit using commercially available phenol formaldehyde–coated glass fibers of 3.2 μ diam has been designed for removing a trace quantity of dispersed oil from water. It was tested on both a synthetic stream and on an actual industrial effluent stream. The influent stream contained 85–100 ppm by volume of oil, and the effluent contained an average of 1 ppm by volume of oil. Thus oil removal efficiency of essentially 100% was obtained at a superficial velocity of 1 ft/min. The influent and effluent oil concentrations were measured by both light transmission and light reflectance apparatus. The pressure drop increased from 2 to 25 psi over run times which varied from 14 to 305 hr, owing mainly to accumulation of oil in the bed. Consequently, the removal efficiencies were obtained under unsteady-state conditions. The present design is suitable for large-scale operation by the use of both multiple cells and larger individual cells.

of these secondary emulsions and subsequent separation of the dispersed phase by gravity settling (Treybal, 1963). These include the addition of chemical coagulants, use of alternating electrical fields, and centrifugation. These processes are often expensive and inefficient. The coalescence of the finely dispersed oil drops into large and readily separable drops by passage through a fibrous bed is a very efficient and inexpensive process. However, very little data using pilot scale equipment have been published on the separation of fine oil dispersions with mean drop size of 10 μ such as occurs in actual pollutant streams.

Fibrous bed coalescers, often termed filter/coalescers or filter/separators are presently used extensively to remove water from jet fuel. The literature on filter/separators for jet fuel application has been reviewed by Bitten (1969). Much of the literature available on the filter/coalescers is in the form of patents. The U.S. Patent Office had granted no fewer than 110 patents between 1911 to 1967. The mechanism of the operation of filter/coalescers has been described by Bitten (1969), Davies and Jeffreys (1969), Farley and Valentin (1965), Hazlett (1969a,b), Langdon et al. (1963), Redmon (1963), Sareen et al. (1966). In recent years, efforts have been concentrated on the development of a general mathematical description of fibrous bed coalescer (Fowkes et al., 1970; Sherony and Kintner, 1971a; Spielman, 1968). Sherony (1969) and Spielman (1968) developed mathematical models based on the theory of coagulation and the theory of two-phase flow in porous media, respectively. The literature on coalescence in fibrous bed has been reviewed by Spielman and Goren (1970).

A filter/coalescer is a process which consists of a series of distinct and properly designed operations. The process consists of the following stages:

(a) filtration to remove solid contaminants; (b) preliminary sieving to remove excess and large oil drops; (c) coalescence of fine droplets into a film within and on a finely divided fibrous layer; (d) concurrent lead-off flow of the coalesced film through other fibrous layers of various degrees of fineness and compaction; (e) disengaging layer to allow separation of the film as large oil droplets without reemulsification or graping; (f) separation space between (e) and (g); and (g) lipophobic-hydrophilic second stage for removal of all droplets above a given size, since gravity separation is usually not efficient.

Several finishing stages (c through g) in series to obtain complete removal may be required.

A coalescer/separator unit (stages c through g) of 1-ft^2 active area has been designed for removing dispersed oil from water and has been tested on both a synthetic stream and on an actual pollutant stream. Preliminary tests were carried out using 1.5-in. diam (1.77-in.^{2} active area) plexiglas coalescer cell. Then the design of the 1-ft^2 unit was developed in two stages. In the first stage an operational model was constructed using plastic construction which permitted changes with a minimum of effort and expense. In second stage a metal unit was constructed, the latter with multiple cells, could be used in small-scale demonstration unit at rates of 25–50 gpm.

Final Large-Scale Coalescer Unit

The final coalescer cell, Figure 1, with 144 in.^{2} of active area was constructed of aluminum. The cell consists of (a) fibrous bed assembly (6), which is held between two diffuser plates (5) and (7) and supported by plate (9); (b) frames for influent stream (3), effluent oil (11), and water effluent (15); (c) a standard 100-mesh monel screen (13) coated with 0.005 in. of TFE to separate oil; and (d) end plates (1) and (17). O-ring seals are provided between these members by the frames (2), (4), (8), (10), (12), (14), and (16).

The fiber bed assembly is shown schematically in Figure 2. The glass fiber mats (13), (14), and (15) are clamped between the two perforated plates (3) and (8). The coarse glass entrance (13) and exit (15) layers act as diffusers. The perforated plates are held in place by the two diffuser plates (1) and (10) which consist of $^1/_4$-in. tread plates provided with 144 $^1/_4$-in. holes. The spaces between the treads and the perforated plates are sealed by a poured urethane rubber gasket (2) and (9).

The $^1/_4$-in. overall membrane thickness is maintained by the thickness of the gaskets (4) and (7) and the spacer frame (5). The membrane thickness can be varied by changing the thickness of either the gaskets or the spacer frame.

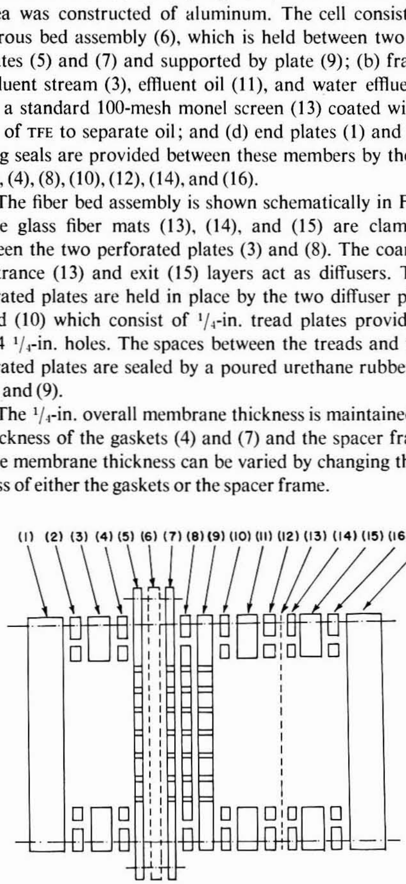

Figure 1. Final coalescer unit

(1) End plate
(2) Seal frame
(3) Entrance frame
(4) Seal frame
(5) Diffuser tread plate
(6) Coalescer bed
(7) Diffuser tread plate
(8) Seal frame
(9) Support plate
(10) Seal frame
(11) Oil effluent frame
(12) Seal frame
(13) 100-Mesh Monel screen coated with 0.005 in. Teflon
(14) Seal frame
(15) Water effluent frame
(16) Seal frame
(17) End plate

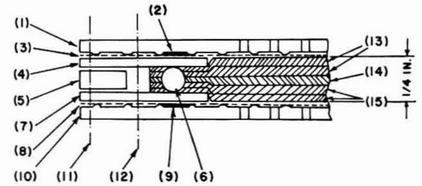

Figure 2. Fibrous bed assembly

(1) Diffuser tread plate
(2) Urethane rubber gasket
(3) Screen support
(4) Gasket
(5) Spacer frame
(6) Metal O-ring
(7) Gasket
(8) Screen support
(9) Urethane rubber gasket
(10) Diffuser tread plate
(11) Outside bolt square, eight $^1/_2$-in. diam holes
(12) Inside bolt square, thirty-two $^5/_{16}$-in. diam holes
(13) 10.1-μ coarse glass fiber layer
(14) 3.2-μ fine glass fiber layer
(15) 10.1-μ coarse glass fiber layer

The membrane edge is sealed by the metal O-ring (6) which is $^1/_8$ in. in cross-sectional diam.

The fibrous bed assembly was bolted together through $^1/_2$-in. holes using $^3/_8$-in. bolts.

The glass fiber membrane is formed from standard (used in water/jet-fuel application) phenol formaldehyde–coated glass fiber and consisted of the three layers: (a) 2 in. of 10.1 μ glass, 0.6 lb/ft^3 nominal density; (b) a coalescer layer of $^1/_2$ or 1 in. of 3.2 μ glass, 0.6 lb/ft^3 nominal density; (c) 2 in. of 10.1 μ glass, 0.6 lb/ft^3 nominal density worked as a disengaging layer. These fibers were Owens-Corning Aerocor, 10.1 μ, and FM-004, 3.2 μ. The physical properties of these fibers are given in Table I. The glass fiber membrane was compressed to overall thickness of $^1/_4$ in. The coalescer layer (14) in most tests was 0.05 in. thick, 12 lb/ft^3 dense, with 92% void fraction.

Materials

The industrial effluent material containing 40–50 ppm of oil was obtained from the hot mill cooling water treatment system at Interlake Steel Corp. No. 30 grade automotive lubrication oil and, after solvent extraction, pollutant oil from a skimming tank at Interlake Steel Corp. were used to make the synthetic dispersions for a majority of tests in the laboratory. In all cases the oil to be separated was diluted with an equal volume of kerosene, a necessary treatment to reduce the viscosity of the separated oil phase in order for it to flow through the fiber bed. The physical properties of these materials are given in Table II.

Table I. Physical Properties of the Fibers

Fine glass fiber (pink) Owens Corning FM-004

Size distribution			
Interval, μ	No. of fibers	Weight	Density, g/cm^3
1–2	11	0.025 lb/ft^2	2.57 ± 0.02
2–3	11		
3–4	18		
4–6	8		
6–8	2		
8–10	0		
	50		
Mean diam = 3.2 μ			
Coarse glass fiber (yellow) Owens Corning Aerocor			
1–3	2		2.57 ± 0.02
3–5	5		
5–7	4		
7–10	17		
10–15	18		
15–25	3		
>25	1		
	50		
Mean diam = 10.1 μ			

Test Assembly

The test assembly is shown schematically in Figure 3. It consists of four major components mounted on dollies: filter/coalescer, feed tank, pumping system, and kerosene pumping system.

The feed tank unit consists of a stirred 75-gal. tank (10). Excess water is added to the internal overflow tank (13). The latter automatically adds any necessary volume of makeup water. The system temperature is maintained at any constant value by varying the amount of water to drain (ml/min to gpm) and thus the amount of cold water makeup. Normally the pump suction is via line (9) to which the oil feed is added directly via line (8). In the case of an actual pollutant, the latter is added to the tank and put through the system with an effluent from cell returned to tank. Thus the pollutant concentration varies as a first-order reaction and may be evaluated over an hour with decreasing inlet concentration rather than in 7 min with once-through flow. The kerosene solvent which is added to the suction line (9) does not enter the tank or interfere with the evaluation. In preliminary tests, oil was added batchwise to the tank every $^1/_2$ hr so that influent concentrations would vary between 100 to 25 ppm or otherwise as desired.

The standardized emulsion was produced by passage through liquid ring pump (1) operating at 3450 rpm. The oil feed is added by a zenith pump (7) driven by a variable speed Graham transmission. A 5-μ cartridge filter (5) was used in several tests (No. 1 and 4, Table III) to prevent plugging of the bed. Depending on length of use, the 5-μ filter cartridge would coalesce from 50 to 5% of the entering emulsion.

The oil concentration in the influent and effluent was determined by light transmission apparatus. The details of the

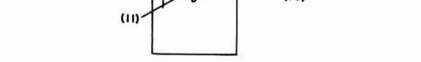

Figure 3. Test assembly

(1) Liquid ring pump
(2) Bypass line
(3) Feed line
(4) Flow indicator
(5) 5-μ cotton filter
(6) Oil feed tank
(7) Zenith pump for oil feed
(8) Oil feed line
(9) Pump suction line
(10) 75-Gal. polyethylene tank
(11) Stirrer
(12) Makeup water
(13) Internal overflow tank
(14) Overflow to drain
(15) Cell inlet
(16) Inlet sample valve
(17) Coalescer cell
(18) Pressure indicator
(19) Oil and air vent valve
(20) Oil and air vent valve
(21) Pressure indicator
(22) Outlet sample valve
(23) Cell effluent

Table II. Physical Properties of the Materials Used

Material	σ^{a}_{12}, dynes/cm	ρ^{b}_{d}, g/cm³	μ^{c}_{d}, g/cm sec	μ^{d}_{c}, g/cm sec	Temp, °F
Kerosene	37.8	0.816	0.0191	0.0092	75 ± 2
1/1 No. 30 oil/kerosene	23.7	0.840	0.2320	0.0092	75 ± 2
1/1 ILS oil/kerosene	17.5	0.860	0.3600	0.0092	75 ± 2

[a] Interfacial tension.
[b] Density of the dispersed phase (oil).
[c] Viscosity of the dispersed phase (oil).
[d] Viscosity of the continuous phase (water).

Table III. Summary of Test Results with Aluminum Cell

Run No.	Oil	In.[a] Uncom. Fibers 10.1 μ/3.2 μ/10.1 μ	Compressed[b] density, lb/ft³	Flow rate, gpm	Temp, °F	Press. drop, psi	Time, hr	At ΔP=25 psi		Tank	Influent	Effluent	Remarks
								gal.[c]	hr				
1	K[d]/# 30	2/1/2	12.0	7.5	~80	9.0	13.0	15,400	34	...	13–80[e]	0[e]	with 5-μ filter
2	K/# 30	2/½/2	10.8	7.5	~70	19.5	47.0	23,500	52	...	85[e]	0[e]	
3A	K/P[f]	2/½/2	10.8	7.5	~80	6.0	½	...	...	29–12[g]	40–20[g]	0[e]	ILS[h] sand filter
3B	K/P	2/½/2	10.8	7.5	...	...	⅙	...	...	30–20[g]	47–30[g]	0[e]	ILS backwash overflow
4	K/P	2/½/2	10.8	7.5	~80	7.0	⅔	...	...	27–13[g]	10[e]	0[e]	ILS backwash overflow with 5-μ filter
5A	K	2/½/2	10.8	1.87	68	11.5	24	4,000	36	...	85[e]	3[e]	Excess cooling water
5B	K	2/½/2	10.8	1.87	~85	8.3	97	34,200	305	...	85[e]	3[e]	
6	K	2/½/2	10.8	7.5	64	18.8	10	6,300	14	...	85[e]	3[e]	
7	K	2/½/2	10.8	7.5	85	17.9	68.5	67,700	151	...	85[e]	2[e]	

[a] Nominal thickness, in. of 10.1 μ/3.2 μ/10.1 μ fibers.
[b] Compressed density, lb/ft³.
[c] Extrapolation by linear ratioing last point.
[d] Kerosene.
[e] Ppm.
[f] Pollutant.
[g] TU.
[h] Sample of pollutant stream from Interlake Steel Corp.

apparatus are given by Sherony (1969, 1971b). The calibration of the light transmission device is given in Figure 4. Kerosene, which gave comparable results for systems tested, was used as a dispersed phase for calibration. A Model 2100A Hach turbidimeter was also used in some cases to determine influent and effluent turbidity which is a measure of oil concentration. For a particular system subjected to particular mixing action, both methods are very reproducible in low concentration (Bitten et al., 1964). The effluent drop size distribution was not determined. Finely dispersed dirt particles have been found to give very high apparent oil concentration (Bitten et al., 1964).

Results and Discussion

Preliminary Tests. LABORATORY COALESCER CELL. Tests were conducted using 1.5-in. diam (1.77-in.² active area) cell, at velocities of 0.15 to 1.96 ft/min with influent oil concentrations of 50 and 500 ppm. The synthetic oil dispersions consisted of kerosene blended with 0, 9, 33, and 50% of No. 30 motor oil and 50% of skimmed oil (used after solvent extraction treatment) obtained from Interlake Steel Corp. With a coalescer layer of 5/16 or 5/64-in. length and about 11.6-lb/ft³ density, oil in the effluent stream varied from 7 ppm to generally nondetectable oil for all systems at all velocities investigated. Decreasing the density of coalescer layer to 5.9 and 8.7 lb/ft³, under similar operating conditions, resulted in poor oil removal efficiency.

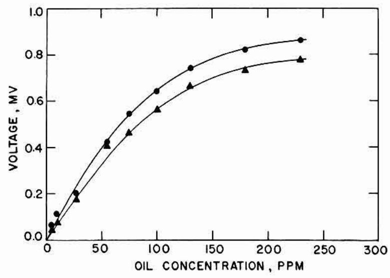

Figure 4. Calibration of light transmission apparatus

System: Kerosene dispersed in water
● Outlet optical cell
▲ Inlet optical cell

Though an oil removal efficiency of almost 100% was obtained, the pressure drop across the bed was found to increase very rapidly with time as shown in Figure 5. In the absence of an oil dispersion (single phase flow of water), however, the pressure drop increased at a very low rate (Figure 5).

LARGE SCALE PLASTIC COALESCER CELL. The main purpose of building the plastic cell was to develop construction techniques. After making numerous construction modifications to

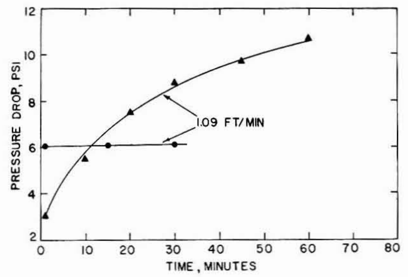

Figure 5. Pressure drop for single- and two-phase flow

Fiber: 3.2-μ glass fiber

● Single-phase (water) flow

Bed density = 15.8 lb/ft^3; bed length = 0.25 in.

▲ Two-phase flow;

Bed density, coalescer layer = 11.80 lb/ft^3; filter layer = 11.00 lb/ft^3; separator layer = 8.90 lb/ft^3

Bed length, coalescer layer = $^5/_{64}$ in., filter layer = $^1/_{16}$ in., separator layer = $^5/_{64}$ in.

Inlet oil concn. $\simeq$ 70 ppm

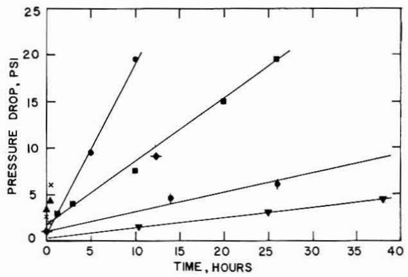

Figure 6. Summary of performance characteristics of 1-ft^2 filter/coalescer (selected points)

-◆- Run 1 at 80°F, 7.5 gpm
■ Run 2 at 70°F, 7.5 gpm
× Run 3 at 80°F, 7.5 gpm
▲ Run 4 at 80°F, 7.5 gpm
▼ Run 5B at 85°F, 1.87 gpm
● Run 6 at 64°F, 7.5 gpm
⧫ Run 7 at 85°F, 7.5 gpm

eliminate internal leakage and nonuniformity of the coalescer bed, performance tests with kerosene and 50% of either No. 30 motor oil or Interlake Steel pollutant oil gave 0–2 ppm oil in the effluent. The pressure drop showed the same high rate of increase as the tests with the small cell. The pressure drop, after treating the cell by backward or forward flushing with high-velocity water, would be reduced to original starting value. However, the bed gave very poor coalescence performance.

Final Tests. The data for the large-scale metal coalescer cell are summarized in Table III and Figure 6. The data are presented in detail in the report by Langdon et al. (1971). These data show that the effluent stream contained 0–3 ppm of oil. The ppm values above zero are probably due to zero point drift in the light transmission instrument. Some individual readings using ILS oil (Langdon et al., 1971) were in the range of 6 ppm. These could be due to finely dispersed red iron oxide (Bitten et al., 1964) which is present in this pollutant. The effluent concentrations appear to be independent of the test variables: thickness and density of 3.2-μ coalescer layer (Runs 1 and 2), velocity through the bed (Runs 5B and 7), temperature (Runs 5A and 5B; Runs 6 and 7), length of run, and pressure buildup.

The pressure drop across the bed increased almost linearly with time as shown in Figure 6. However, the rate of increase was lower at the higher temperature under comparable conditions. The pressure drop can be lowered to the original starting value by removing the oil in situ using solvent extraction, backwash, forward wash, steaming, or combinations thereof. Generally these treatments destroy the coalescing ability of the bed. In two small-scale tests (Langdon et al., 1971), where the fibers were stabilized with a resin to minimize mechanical degradation of fibers, the bed was regenerated in situ several times with solvent treatment. The bed recovered its original characteristics of low pressure drop and coalescence efficiency.

The capacity of the coalescer bed, in gallons of influent with 85 ppm of oil that can be passed through to a pressure drop buildup of 25 psi, was found to be 67,700 gal. at a flow rate of 7.5 gpm (1 fpm superficial velocity) and a temperature of 85°F (Run 7). Lowering the influent temperature to 64°F lowers the capacity to 6300 gal. (Run 6), which is approximately 10% of that at 85°F. Similar observation was made at a flow rate of 1.87 gpm ($^1/_4$ fpm) (Runs 5A and 5B). The capacity, however, at the same temperature for the flow rate of 7.5 gpm was only approximately two times greater than that at 1.87 gpm (Runs 5A and 6; Runs 5B and 7).

The tests with actual pollutant material from Interlake Steel Corp. (Runs 3 and 4) showed less than 2 ppm oil in the effluent. However, the backwash overflow (Run 4) required a 5-μ filter in the line to remove dirt which otherwise plugged the fiber bed. This filter removes some large oil drops but most of the dispersed oil passed through without coalescing.

Conclusions

A 1-ft^2 coalescer cell using filter press construction has been designed and tested on a synthetic oil dispersion and on an actual pollutant stream. The commercial fibers, with phenol formaldehyde coatings and a fiber diam of 3.2 μ, gave oil removal efficiency of almost 100% at a flow rate of 7.5 gpm (1 fpm superficial velocity) over the entire run time. The large rate of pressure increase, observed in our work and unreported by other investigators, is due mainly to oil accumulation in the bed and probably to a minor extent to mechanical degradation of the fibers. It is definitely not due to solid particulate contamination except to a minor extent in long-term tests with once-through operation.

The controlling parameter for a practical unit appears to be the life of the bed which is arbitrarily defined in the present work as the throughput up to the point where the pressure drop reaches 25 psi. The present coalescer design may be used as is and readily scaled up either by using multiple cells or by increasing the area of individual cells. The capacity, corresponding to a pressure drop of 25 psi, for a flow rate of 7.5 gpm was found to be 67,700 gal. for a stream at 85°F and 6300 gal. for a stream at 64°F. These capacities while low do not preclude practical operations since it is a simple matter to install new fiber beds.

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Dissipation of Pesticides from Soil by Volatilization of Degradation Products

I. Lindane and DDT

Mark M. Cliath and William F. Spencer[1]

USDA, Agricultural Research Service, Soil and Water Conservation Research Division, University of California, Riverside, Calif. 92502

■ Volatility of the primary degradation products of lindane and DDT were compared with volatility of the parent compounds. The primary degradation products of lindane and DDT—PCCH and DDE—have much higher vapor pressures than the parent compounds. At 30°C, the vapor density of PCCH was 13.7 times that of lindane; the vapor density of *p,p′*-DDE was eight times that of *p,p′*-DDT. With lindane, calculations verified by laboratory or field measurements of relative volatility indicate that two thirds to three fourths of the volatilized material is lost as PCCH from a calcareous soil. Field measurements of atmospheric concentrations of DDT compounds agreed with predictions of relative volatility from laboratory vapor density measurements. Sixty-six percent of the total DDT atmosphere over a field containing residual DDT was *p,p′*-DDE. This means that most of the *p,p′*-DDT now present in well-aerated soils probably will be volatilized as *p,p′*-DDE. The presence of degradation products in significant amounts in field soils indicates that volatilization of degradation products, such as PCCH and DDE can be a major pathway for loss of some organochlorine insecticides from soil.

Pathways for the loss of pesticides from soils have been extensively investigated. Volatilization, leaching, metabolic and nonmetabolic degradation are mechanisms which contribute to their loss (Edwards, 1966). Organochlorine insecticides are among the most persistent pesticide chemicals, but their volatilization from the soil surface is a major pathway for loss from the soil. This involves desorption of the pesticide from the soil, diffusion upward to the soil surface and volatilization of the compounds into the atmosphere. Rate of loss by volatilization is related to vapor pressure of the chemical (Farmer et al., 1972; Guenzi and Beard, 1970; Spencer, 1970; Spencer and Cliath, 1970b). Since vapor pressures of the organochlorine insecticides are relatively low, volatilization may occur over a long period of time. This provides opportunities for degradation products to form in the soil. For example, *p,p′*-DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] breaks down in soil to *p,p′*-DDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene], *p,p′*-DDD [1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane], and other compounds (Edwards, 1966). Spencer and Cliath (1972) reported that the vapor pressure of *p,p′*-DDE was several times greater than that of *p,p′*-DDT. Yule et al. (1967) reported that lindane (γ-1,2,3,4,-5,6-hexachlorocyclohexane) decomposed in soil to PCCH (γ-1,3,4,5,6-pentachlorocyclohexene). Cliath and Spencer (1971) found that lindane disappeared much more rapidly than dieldrin from two irrigated soils, and PCCH was found in plots to which lindane had been applied, suggesting that some of the lindane was converted to PCCH in the alkaline soil.

The purposes of this paper are to report data on the rate of formation of PCCH from lindane and DDE from DDT; to report data on relative volatility of the degradation products compared with that of the parent compounds; and to present evidence which indicates that volatilization of degradation products, such as PCCH and DDE, can be a major pathway for loss of some organochlorine insecticides from soil.

Methods and Materials

Lindane. Spencer and Cliath (1970a,b) measured the vapor pressure of lindane and the desorption of lindane from soil by a gas saturation method in which N_2 gas was passed through insecticide-treated glass bead or soil columns at a sufficiently slow rate to ensure equilibrium vapor saturation. The same columns and procedures were used to measure rate of formation of PCCH and its vapor pressure, with and without soil.

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[1] To whom correspondence should be addressed.

The vapor pressure, or saturated vapor density, of PCCH was determined in the lindane-treated pyrex glass bead columns. One or two grams of lindane was applied to 1000 grams of beads. The beads had a high residual alkalinity (a water suspension pH of 10.4) which caused sufficient quantities of lindane to be degraded to PCCH during the measurement of lindane vapor density to provide saturation vapor densities for PCCH.

For soil columns, Gila silt loam was treated with 5, 10, 25, and 50 μg/g of 100% lindane, the soil water content was adjusted to 10% water, and vapor density measurements were made in triplicate at various temperatures over a 47-day period. Lindane and PCCH vapor densities were measured periodically, as previously reported for lindane (Spencer and Cliath, 1970a, b). Each vapor density measurement required 1 to 2 days for vapor collection with a flow rate of 3–5 ml/min. The soil was assayed for PCCH and lindane following the last vapor density measurement at 40°C.

Movement and persistence of dieldrin and lindane were measured in two calcareous, low-organic-matter soils, with and without irrigation. The procedures and results have been described (Cliath and Spencer, 1971). Briefly, the insecticides were uniformly mixed within the 0- to 7.5- or 7.5- to 15-cm depth by excavating the soil, mixing the soil and insecticides in a cement mixer, and placing the treated soil back in the excavation. Recovery of the added insecticides was measured one year and two years after application. Concentrations of PCCH, the primary degradation product of lindane, as high as 2.5 μg PCCH/g of soil were observed in the soil extracts. The distribution of lindane and PCCH in Holtville fine sandy loam was studied in detail. This soil is a calcareous soil with adsorption characteristics similar to Gila silt loam used in the vapor density studies. The clay and organic matter contents of the two soils were 17.5 and 0.4% for the Holtville fine sandy loam and 18.5 and 0.6% for the Gila silt loam. The ratio of PCCH/lindane volatilizing from the field was estimated from relative vapor pressures and the amounts of PCCH and lindane in the field soil following lindane addition.

DDT. Spencer and Cliath (1972) recently measured the vapor pressures of DDT and some degradation products by a gas saturation method. They reported that the vapor pressure of *p,p′*-DDE was several times greater than that of *p,p′*-DDT. To study rate of formation of DDE from DDT as related to time after addition of DDT to soil, 10 μg/g of either *p,p′*-DDT or *o,p′*-DDT[1,1,1-trichloro-2-(*p*-chlorophenyl)-2-(*o*-chlorophenyl)ethane] was applied to Gila silt loam. The insecticides were added in hexane to autoclaved Gila silt loam, the hexane evaporated, water content adjusted to 7.5%, and the soil placed in glass columns. Vapor density measurements for DDT and DDE were started 10 days after DDT was added to the soil by a gas saturation method as previously described (Spencer and Cliath, 1972). Temperature was controlled at 30° ± 0.2°C.

Volatilization of DDT and related compounds was measured in the field to verify predictions of potential volatilization rates from the laboratory measurements of relative vapor pressures. Atmospheric concentrations of DDT and related compounds were measured over a field in Coachella Valley, Calif., in June 1971. The well-aerated soil in the field contained high amounts of residual DDT from past applications of technical DDT to sweet corn for earworm control. Technical DDT had been applied over a seven-year period, usually as a dilute emulsion at the rate of 3 lb DDT/acre, 10–12 times per year, with the last application in the spring of 1970. The vapor collection system was similar to that used in vapor pressure measurements, but with gas-washing bottles containing ethylene glycol as the vapor trapping agent instead of hexane as used in the laboratory. Two traps were located at 30 and two at 76 cm above the soil surface. Air was drawn through the traps at the rate of 3–5 l./min with a vacuum pump powered by a portable generator. The soil was a calcareous loamy sand with less than 1% organic matter. The field was irrigated two days prior to sampling and was freshly disked just before sampling. Therefore, the soil surface was moist and conducive to maximum volatilization of the insecticides from the soil. The first sampling period was for 15 hr, 1500–0900 hours, and the second for 24 hr, beginning at 0900 hours the second day after disking.

The insecticides were extracted from the ethylene glycol with hexane. Concentrations of *o,p′*- and *p,p′*-isomers of DDT, DDE, and DDD were determined in the hexane extracts by glc.

Standards and Analytical Methods. Lindane (100% γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane), *o,p′*-DDT and *p,p′*-DDT of better than 99% purity were used. The primary degradation product of lindane, PCCH, was synthesized using a modified Nakijima method (Nakijima et al., 1949). The vacuum-distilled product was purified by elution through an activated acid alumina column, using an ethyl ether–pentane mixture as the eluant. The pure fraction was isolated by monitoring each 5-ml eluate with a rapid-scan ir. Identity of the compound was verified by nmr (proton-ratio method). Using glc, the product was found to be better than 99% pure.

All samples were analyzed using a Beckman GC-5 gas-liquid chromatograph equipped with a nonradioactive electron-capture detector.

Results and Discussion

Lindane. The measured vapor density and calculated vapor pressure of PCCH on glass beads and a comparison with the vapor density of lindane at three temperatures are shown in Table I. The apparent vapor pressure of PCCH was linearly related to temperature by the equation: $\log_{10} P = 19.481 - (6.717/T)$. The saturated vapor density of PCCH was much higher than that of lindane, and the vapor density ratio, PCCH/lindane, increased with temperature, indicating that the vapor density of PCCH increased more rapidly with temperature than did that of lindane.

The ratio of PCCH/lindane vapor density in Gila silt loam increased with successive measurements on the same columns, indicating that lindane was being continuously degraded to PCCH in soil. The concentrations of PCCH and lindane in the soil at the termination of vapor density measurements and the average vapor density of PCCH and lindane for the last two measurements at 40°C are shown in Table II. The mean

Table I. Vapor Pressure of PCCH and Saturation Vapor Density, d_0, of PCCH and Lindane (γ-BHC) at Various Temperatures

Temp, °C	Vapor press.,[a] PCCH mm Hg × 10^{-3}	Vapor density, d_0		
		PCCH, μg/l.	Lindane,[b] μg/l.	Ratio, PCCH/ lindane
20	0.395	5.29	0.518	10.2
30	2.00	27.0	1.97	13.7
40	11.9	149	6.78	22.0

[a] Calcd from vapor density, d_0, with the equation $p = d_0 \cdot RT/M$.
[b] From Spencer and Cliath (1970a).

Table II. Vapor Density of PCCH and Lindane at 40°C as Related to Concentrations of Each in Gila Silt Loam at 10% Water Content

Lindane added, μg/g	Soil concn[a] Lindane, μg/g	Soil concn[a] PCCH, μg/g	Soil concn[a] Ratio, PCCH/lindane	Vapor density[b] Lindane, μg/l.	Vapor density[b] PCCH, μg/l.	Vapor density[b] Ratio, PCCH/lindane
5	4.0	0.46	0.114	0.32	0.78	2.44
10	7.8	0.93	0.119	0.51	1.56	3.06
25	20.4	2.47	0.121	2.19	5.30	2.42
50	41	4.51	0.110	4.87	12.36	2.54
Mean	. . .	. . .	0.116	. . .	. . .	2.62

[a] Measured after vapor density measurements at various temperatures over a 47-day period.
[b] Av of last two vapor density runs made at 40°C.

ratio of PCCH/lindane in soil of 0.116 resulted in a mean vapor density ratio of PCCH/lindane of 2.62. This vapor density ratio is in close agreement with ratios predicted from desorption isotherms for lindane and saturation vapor densities of PCCH and lindane. Spencer and Cliath (1970b) found that desorption isotherms for lindane on Gila silt loam relating vapor density, d/d_0, to soil concentration followed the Freundlich equation:

$$\frac{x}{m} = k'\left(\frac{d}{d_0}\right)^{\frac{1}{n}} \qquad (1)$$

where d is the observed vapor density and d_0 is the saturation vapor density without soil; k' and n are constants, and x is the weight of adsorbate taken up by a weight m of solid. In this case, k' is numerically equal to the x/m value when d/d_0 equals unity, or the soil concentration when a saturated vapor density is present. Since $1/n$ is usually very close to unity, adsorption isotherms are closely approximated by assuming a linear relationship between soil concentrations and relative vapor density. It follows, then, that the ratio of the vapor density of PCCH (2)/lindane (1), or for any other two closely related chemicals (1) and (2), can be calculated with the equation:

$$\frac{d_2}{d_1} = \frac{(k')_1}{(k')_2}\cdot\frac{(x/m)_2}{(x/m)_1}\cdot\frac{(d_0)_2}{(d_0)_1} \qquad (2)$$

if saturation vapor densities (d_0) of the two compounds and their soil concentrations (x/m) are known.

Assuming the same desorption coefficient k' for PCCH and lindane and using the mean PCCH/lindane soil concentration ratio of 0.116 (Table II) in Equation 2, the predicted PCCH/lindane vapor density ratio would be 2.55. This is in close agreement with the observed value of 2.62 and indicates that soil adsorption isotherms for PCCH and lindane are similar. Therefore, predictions on relative volatilization of PCCH and lindane are possible from known soil concentrations of each. For example, with equal concentrations of PCCH and lindane in soil, the vapor density ratio PCCH/lindane would be the same as the saturation vapor density ratios in Table I—i.e., at 30°C the vapor density of PCCH would be 13.7 times that of lindane.

Distribution of lindane in the field plots as affected by placement and irrigation were previously reported (Cliath and Spencer, 1971). An example of vertical distribution patterns for PCCH and lindane and the ratio of PCCH/lindane in Holtville fine sandy loam one year after application of 20 μg/g lindane at the 7.5- to 15-cm depth are shown in Figure 1. The ratio of PCCH/lindane was greater away from the treated zone than in the treated zone. For example, 3.9 times more PCCH than lindane was present in the surface 2.5 cm. This suggests that PCCH is more mobile than lindane. The ratio of PCCH/lindane within the 7.5- to 15-cm treated zone after 6 months, 1 year, and 2 years did not drop below 0.16 in plots receiving monthly irrigation (Table III). The PCCH/lindane ratio was 0.11 or greater in the nonirrigated plots during the same two-year period.

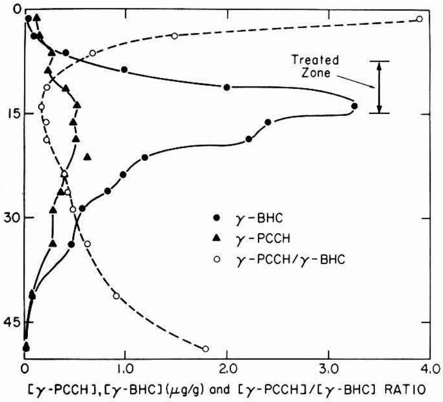

Figure 1. Distribution of PCCH and lindane (γ-BHC) and the ratio of PCCH/lindane in Holtville fine sandy loam one year after application of 20 μg/g lindane at the 7.5–15 cm depth

Calculations using Equation 2 indicate that the mean PCCH/lindane ratio of 0.15 observed after one and two years would result in a PCCH/lindane vapor density ratio of 1.5, 2.1, and 3.3 at 20°, 30°, and 40°C, respectively. This means that for every 100 molecules of the original material volatilized from the soil at 30°C, for example, at least 70 molecules would be the degradation product PCCH. In the field, with variable temperature conditions, probably two thirds to three fourths of the applied lindane which volatilized was lost as PCCH from this calcareous soil.

DDT. The saturation vapor density of *p,p′*-DDT and *p,p′*-DDE at 30°C is 13.6 and 109 ng/l., respectively (Spencer and Cliath, 1972). Thus, the vapor density of *p,p′*-DDE is eight times that of *p,p′*-DDT. Linear desorption isotherms described the relationship observed between relative vapor density, d/d_0, of *p,p′*-DDT and *o,p′*-DDT and concentrations of each in Gila silt loam (Spencer and Cliath, 1972). The linear desorption coefficient, k', in the equation $x/m = k'(d/d_0)$ was 15 and 39 for *p,p′*-DDT and *o,p′*-DDT, respectively, indicating a saturation vapor density of *p,p′*-DDT or *o,p′*-DDT was reached at concentrations of 15 or 39 μg/g. If one assumes similar desorp-

Table III. Ratio of PCCH/Lindane Within the 7.5–15-cm Treated Zone at Various Times After Application of 20 µg/g Lindane to Holtville Fine Sandy Loam

Time after application, months	Irrigated monthly	Nonirrigated	Mean
6	0.17	...	...
12	0.18	0.11	0.15
24	0.16	0.14	0.15

tion isotherms for *p,p'*-DDE and *p,p'*-DDT ($k'_1/k'_2 = 1$), the ratio of *p,p'*-DDE/*p,p'*-DDT in the vapor phase can be estimated from relative concentrations of each in any soil using Equation 2. For example, if equal concentrations of *p,p'*-DDE and *p,p'*-DDT are found in soil, as reported by Swoboda et al. (1971), the concentration of *p,p'*-DDE in the vapor phase in and above the soil will be eight times greater than that of *p,p'*-DDT. Consequently, of every 100 molecules that escape from the soil into the atmosphere, approximately 90 will be DDE molecules. The magnitude of k'_1 and k'_2 will change with soil properties, but the ratio of k'_1/k'_2 should be relatively constant for any pair of closely related compounds. Thus, the vapor density ratio of *o,p'*- to *p,p'*-DDT can be calculated for other similar soils using the k'_1/k'_2 ratio of 0.385 observed for *p,p'*- and *o,p'*-DDT adsorbed on Gila silt loam.

The increase in vapor density of *p,p'*-DDE with time following application of 10 µg/g *p,p'*-DDT to Gila silt loam at 7.5% water and 30°C is shown in Figure 2. Sufficient DDT was hydrolyzed in this calcareous soil to increase the vapor density of *p,p'*-DDE from 0 to 1.4 ng/l. after 65 days. The use of autoclaved soil and a N_2 gaseous atmosphere for the vapor density measurements probably restricted the rate of formation of DDE. During this same period, the vapor density of *p,p'*-DDT did not measurably decrease, indicating that only small amounts of *p,p'*-DDE were formed in the soil. According to Equation 2, less than 0.24 µg/g *p,p'*-DDE would be sufficient to produce the 1.4 ng/l. vapor density measured after 65 days.

No *o,p'*-DDE [1,1-dichloro-2-(*p*-chlorophenyl)-2-(*o*-chlorophenyl)ethylene] was detected in the N_2 atmosphere passing through soil columns containing *o,p'*-DDT. Evidently, hydrolysis of *o,p'*-DDT to *o,p'*-DDE proceeds much more slowly than that of *p,p'*-DDT to *p,p'*-DDE.

The concentrations of *p,p'*-DDT, *p,p'*-DDE, *o,p'*-DDT, and *o,p'*-DDE in the atmosphere over a field previously treated with technical DDT are presented in Table IV, along with data on soil concentrations of each compound. The atmospheric concentrations are relatively high considering that DDT had not been applied for approximately 14 months. The average total atmospheric concentration was 496 ng/m³ during the first 39-hr period following disking of the field.

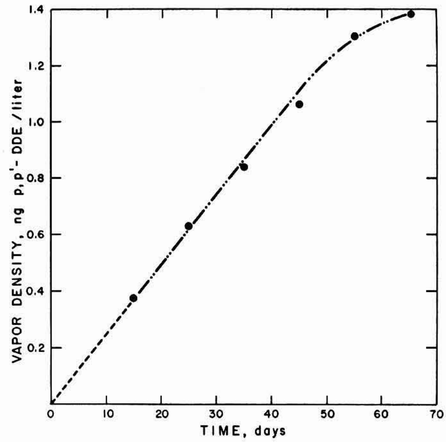

Figure 2. Increase in vapor density of *p,p'*-DDE with time following application of 10 µg/g *p,p'*-DDT in Gila silt loam at 7.5% water and 30°C

The atmospheric concentrations were higher during the first measurement period immediately after disking than on the second day after disking. This was probably due to a combination of surface depletion of the chemicals and surface drying of the soil. There was no measurable difference in atmospheric concentrations between the 30- and 76-cm sampling heights.

Atmospheric concentrations of *p,p'*-DDE were much higher than those of *p,p'*-DDT. The concentration of *o,p'*-DDT was about 60% as great as that of *p,p'*-DDT, in spite of the fact that much lower quantities of *o,p'*-DDT were present in the soil than *p,p'*-DDT. The mean atmospheric concentration ratios of *p,p'*-DDE/*p,p'*-DDT and of *o,p'*-DDT/*p,p'*-DDT are in close agreement with the ratios predicted with Equation 2 from soil concentration ratios and relative vapor densities. The ratio of *p,p'*-DDE/*p,p'*-DDT was calculated with Equation 2 assuming similar desorption isotherms or $k'_1/k'_2 = 1$, whereas the ratio of *o,p'*-DDT/*p,p'*-DDT in the atmosphere was calculated using the value of $k'_1/k'_2 = 0.385$ observed for the two isomers adsorbed on Gila silt loam (Spencer and Cliath, 1972). Of the total DDT atmosphere, 66% was *p,p'*-DDE and

Table IV. Soil and Atmospheric Concentrations of *p,p'*-DDT, *p,p'*-DDE, *o,p'*-DDT, and *o,p'*-DDE and the Ratio of Each to *p,p'*-DDT in a Field Containing Residual Technical DDT

	In soil		In atmosphere						
			Run 1[a]		Run 2[b]		Mean		
		Ratio to *p,p'*-DDT		Ratio to *p,p'*-DDT		Ratio to *p,p'*-DDT		Ratio to *p,p'*-DDT	
Chemical	µg/g		ng/m³		ng/m³		ng/m³	meas	calcd[c]
p,p'-DDT	14.1	1.0	104	1.0	78	1.0	91	1.0	...
p,p'-DDE	6.2	0.44	419	4.03	235	3.01	327	3.52	3.56
o,p'-DDT	2.7	0.19	69	0.66	44	0.56	57	0.61	0.55
o,p'-DDE	0.12	0.008	26	0.25	17	0.22	22	0.24	...
Total	23.1	...	618	...	373	...	496	...	...

[a] Av of three samples collected at 30- and 76-cm heights during a 15-hr period immediately after disking.
[b] Av of four samples collected at 30- and 76-cm heights during a 24-hr period beginning 1 day following disking.
[c] Calcd with Equation 2 from soil concentration ratios and saturation vapor densities.

for every 100 molecules of *p,p'*-isomers volatilizing from the soil surface, approximately 80 were *p,p'*-DDE at this soil concentration. These data support the contention that most of the *p,p'*-DDT now present in well-aerated soils will be volatilized as *p,p'*-DDE. Under field conditions, volatilization proceeds over a long time period, and the actual amounts and kinds of chemicals lost into the atmosphere may be quite different from those measured in short-term volatilization studies. In most soils, *o,p'*-DDT is less persistent than *p,p'*-DDT, as noted herein. Where the reverse has been observed (Lichtenstein et al., 1971), the lower persistence of *p,p'*-DDT is probably due to greater conversion of *p,p'*-DDT to *p,p'*-DDE and subsequent volatilization of the *p,p'*-DDE.

The ecological significance of the greater volatility and, consequently, mobility of *p,p'*-DDE than *p,p'*-DDT has not been ascertained. The presence of *p,p'*-DDE in the biosphere is now of much concern to biologists. Possibly, *p,p'*-DDE is the main organochlorine compound that causes eggshell thinness (Ratcliffe, 1970; Cade et al., 1971). The use of DDT has been considerably curtailed in the U.S., but, due to its persistence, DDT will be present in the environment for many years. Under aerobic conditions, much of the DDT now in soils will be degraded to DDE, which in turn does not readily degrade in soil (Burge, 1971). The vaporization of such degradation products will increase as their concentration in the soil increases. Consequently, it is logical to conclude that most of the residual DDT now in well-aerated soils will eventually be lost from the soil as DDE. It is conceivable that much of the harmful effects from the use of DDT has been due to the more volatile breakdown product, DDE. Soil and water management practices can be used to alter the pathway of breakdown of DDT in soil. For example, under oxygen-deficient conditions, caused by flooding and organic matter treatments, DDT is degraded to DDD and other water-soluble metabolites (Guenzi and Beard, 1967). Field experiments are now in progress to evaluate such soil and water management practices for preferentially degrading the residual DDT to DDD, thereby changing the ratio of the various compounds evaporating from the soil surface.

For lindane and DDT, degradation products have higher vapor pressures than the parent compounds; therefore, higher mobilities through the soil profile and greater volatilization rates into the atmosphere above the soil. Apparently, this is an important pathway for loss of the applied material and other pesticides and their degradation products should be considered with this pathway in mind. This could be a much more important pathway for dissipation of pesticides from soil than direct loss of the applied material.

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Fate of DDT in Severn Estuary Sediments

Eric S. Albone, Geoffrey Eglinton,[1] Nigel C. Evans, Judith M. Hunter, and Michael M. Rhead
Organic Geochemistry Unit, School of Chemistry, University of Bristol, Bristol, BS8 1TS, England

■ The functions of estuarine sediments as pollutant sink and as pollutant bank are assessed in relation to the fate of DDT in the environment. *p,p'*-DDT was degraded more slowly when incorporated in situ in Severn estuary sediments than when incubated in sediment samples maintained under hydrogen in the laboratory. These transformations are compared with the more extensive degradation of DDT on incubation in anaerobic sewage sludge. In all incubations, metabolites included *p,p'*-DDD. The wider application of the techniques developed is discussed.

The degradation of *p,p'*-DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] in Severn estuary sediments has been studied as part of a survey of the transformations undergone by organic compounds in this environment (Albone et al., 1971; Rhead et al., 1971). The Severn estuary drains one sixth of the total land area of England and Wales, including areas of orchard land where DDT has been used (Department of Education and Science, 1969).

Although the use of organochlorine pesticides in Britain is only 55 × 10^4 kg/year, it has been estimated that Britain's rivers annually transport some 1 × 10^4 kg of these compounds to the sea at levels averaging 180 ppb (Agricultural Research Council, 1970; Croll, 1969). Elsewhere in the world where pesticide usage is more intensive, rivers, particularly at time

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[1] To whom correspondence should be addressed.

of flood, may bear heavy burdens of these compounds (Haderlie, 1970). Organochlorine pesticides, being strongly adsorbed on soil and other particulate material (Shin et al., 1970), are likely to be associated with the suspended particulate loads of rivers and so to become incorporated into estuarine sediments (Royal Commission on Environmental Pollution, 1971) which thus act as potential pollutant banks for the surrounding environment. Gas chromatographic evidence obtained in this laboratory suggests the presence of *p,p'*-DDT at a level of 1.9 ppb in the upper layers of sediment in the Severn estuary (at National Grid Reference ST370811).

Using anaerobic sewage sludge, Hill and McCarty (1967) have demonstrated the rapid degradation of DDT to DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane]. In anaerobic soil, Guenzi and Beard (1967) showed that *p,p'*-DDT was degraded to *p,p'*-DDD within a month. The DDT to DDD transformation is brought about by a variety of microorganisms in culture (Guenzi and Beard, 1967). Matsumura et al. (1971) have investigated the ability of microbial isolates from lake sediments and water to degrade DDT and have reported the formation of DDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene] and DDNS [1,1-bis(*p*-chlorophenyl)ethane] in addition to DDD. Fries (1972) has reviewed the field of anaerobic degradation of DDT and concluded that little is known with certainty except that DDD is a major degradation product.

The use of sewage bacteria has already been advocated to provide a rapid biodegradability test for insecticides (Halvorson et al., 1971) and while microbiological degradation provides a process by which environmental pollution caused by the widespread use of persistent pesticides may be reduced, detailed studies on the degradation pathway are required to assess the degree of hazard associated with the degradation products.

The accumulation of pesticide residues and other pollutants in estuarine sediments is to be expected (pollutant bank) and in this study the ability of the sediments of a major British estuary to degrade *p,p'*-DDT (pollutant sink) has been investigated. Particularly powerful has been the use of radiolabeled compounds which enables the path of a given compound and its derived products to be followed through an environment (Eglinton, 1969). This technique has been elegantly employed by Metcalf et al. (1971), using ^{14}C-DDT in a model ecosystem.

Experimental

Incubation Environments and DDT Incorporation. In situ incubations of ^{14}C-*p,p'*-DDT were performed in Severn estuary sediments (at National Grid Reference ST 534832) at a depth of 10–13 cm. The site chosen was near high-water mark on a large expanse of mud flat below Spartina salt marsh. A thin layer of gray silt-covered black mud in which incubations were performed. The site was covered by tide for at least an hour each day (salinity range of water, 13–28‰, $AgNO_3$ titration) and the temperature varied between 5° and 25°C. Sediment movement at the estuary site was sufficiently limited to neither bury nor expose the coring tubes left in situ over a period of six weeks. Analyses of the black mud showed it to be alkaline (pH 8.0–8.2) and to contain the clay minerals illite and kaolinite (Phillips 1010/30 X-ray diffractometer). Calcite and α-quartz are also present. The reducing character of the lower mud is evidenced by the levels of available [i.e., available to plants and estimated by extraction procedures laid down in the Ministry of Agriculture, Fisheries and Food/ADAS Standard Methods (1970)] ferric iron (315 ppm) relative to ferrous iron (100 ppm) and by the presence of free hydrogen sulfide (144 ppm). Levels of available inorganic constituents did not appear exceptional for an estuarine environment. The sampling site is known to be in a region where sediments bear total loads (X-ray fluorescence) of lead (200–400 ppm), zinc (500–900 ppm), copper (85–100 ppm), and nickel (40–50 ppm), based on dry weight (Butterworth, 1970). The water content of one sample of upper silt was 53% w/w, and of one sample of lower silt, 36% w/w. The estuary is known to receive a substantial load of untreated sewage, but what effect this has on the character of the sampling site is uncertain.

Details of individual experiments are given in Tables I–III. ^{14}C-*p,p'*-DDT [phenyl ring ^{14}C(u) 67 μCi/mg, 98% radiochemically pure by tlc, Radiochemical Centre, Amersham, Bucks] was mixed in solution as required with cold *p,p'*-DDT (99% pure, Aldrich Chemical Co.) and the chemical purity of the mixture verified by glc and tlc.

For the in situ experiments, a glass tube, 20 × 6 cm, was pushed into the exposed estuarine sediments at low tide and a central core removed from the enclosed mud using a smaller coring tube, 15 × 3.5 cm. ^{14}C-*p,p'*-DDT (5 μCi, 10 mg) dissolved in the minimum volume of ethanol, was dispersed uniformly around the base of the resulting hole and the mud core replaced in position (Gaskell, 1971). After incubation for 46 days, the contents of the large coring tube were transferred to the laboratory and extracted. Whereas in these in situ studies a localized concentration of pesticide was created within the sediment core, in laboratory experiments a more even dispersion of pesticide was achieved.

For comparative laboratory studies, samples of the darker lower mud were collected in coring tubes, 7.5 × 2.5 cm. Estuary water was taken from pools in the vicinity of the sampling point. ^{14}C-*p,p'*-DDT was injected into prepared sediment samples in the laboratory using the following procedure to facilitate even distribution and quantitative injection of pesticide. A slurry of estuarine mud with estuarine water was prepared, weight ratio 3:1, and divided into fractions (50 grams) between a series of sample bottles. While each sample of slurry was kept agitated, yeast extract nutrient (to 0.1% w/w) and DDT were added as indicated in Table II. Yeast extract was not added in all cases. Its use was to facilitate the co-metabolism of the DDT (Focht and Alexander, 1970 a, b). The DDT was added as a fine aqueous suspension produced by rapidly adding a concentrated ethanolic solution of DDT to an excess of rapidly stirred filtered estuary water. After the slurry was allowed to settle, an intact central portion of undisturbed sediment core (ca. 15 grams) was added directly to each bottle. This was to provide a reservoir of microorganisms representative of the estuarine sediment, should any species—e.g., of obligate anaerobe—have been eliminated during sample preparation. The prepared samples were placed immediately in a McIntosh & Fildes anaerobic jar for incubation under hydrogen at 25°C for three weeks.

For incubations in sewage, ^{14}C-*p,p'*-DDT, 250 μl ethanolic solution, was injected below the surface of rapidly stirred anaerobic sewage sludge (pH ~8, 5% w/w solids, from a 35° C anaerobic digestor, Avonmouth Foul Water Treatment Works, Bristol) and incubated under hydrogen at 35°C. The use of a hydrogen atmosphere has the disadvantage that it may influence some of the bacterial activity, but anaerobic conditions are ensured. No evidence of pesticide residues was found in extracts of control samples of sewage sludge and of estuarine mud from the sampling site by glc analysis.

Extraction and Analysis. After incubation, all samples were centrifuged at 26,000 × *g* for 30 min in stainless steel tubes; the water layer was decanted, filtered, and scintillation counted;

Table I. ^{14}C-*p,p'*-DDT Incubations in Situ in Severn Estuary Sediments

Expt no.	^{14}C-*p,p'*-DDT incorporated	Incubation[a] time, days	Wet wt sediment extracted, g	^{14}C recovered,[b] %	Mass ratio[c] *p,p'*-DDT: *p,p'*-DDD	Tlc zones[d] A:B:C
1	5 μCi, 10 mg	46	686	56	48:1	100:0:0
2	5 μCi, 10 mg	46	622	51	13:1	100:0:0
3 (contr)	0,0	...	616	...	...	...

[a] Incubations commenced April 1, 1971.
[b] % ^{14}C recovered based on total incorporated. These data are minimum recovery values as no quench correction was applied.
[c] From glc total extract comparing relative peak areas with those of standard mixture.
[d] From radioscan peak areas following tlc total extract, solvent system I (see text). Zone A, R_f 0.3–0.6; Zone B, R_f 0.1–0.3; Zone C, R_f 0.0–0.1. Zone A includes DDT and DDD.

Table II. ^{14}C-*p,p'*-DDT Incubations in the Laboratory Using Severn Sediments[a]

Expt no.	^{14}C-*p,p'*-DDT incorporated	Incubation time, days	Wet wt sediment used, g	Init DDT level, ppm	^{14}C recovered,[c] %	Label in aqueous phase[b]	Mass ratio *p,p'*-DDT: *p,p'*-DDD[d]	Tlc zones[e] A:B:C
4	5 μCi, 2 mg[f]	21	67	29.9	88	<0.008 μCi	1:1.1	96:1:3
5	5 μCi, 2 mg	21[g]	65	30.7	40	<0.01 μCi	1:3.3	86:7:7
6 (contr)	0,0[f]	21	50	0	...	...	...	...
7 (contr)	0,0	21	50	0	...	...	...	...

[a] Incubations under hydrogen at 25°C.
[b] Activity of filtered aqueous layer obtained on centrifuging incubated sample.
[c,d,e] See notes *b, c, d,* Table I.
[f] Incubations enriched with 0.1% w/w yeast extract ("Yeastrel," Brewer's Food Supply Co.).
[g] Following incubation, air was admitted to this sample and it was allowed to stand a further 36 days.

Table III. ^{14}C-*p,p'*-DDT Incubations in Anaerobic Sewage Sludge[a]

Expt no.	^{14}C-*p,p'*-DDT incorporated	Incubation time, days	Volume sludge used,[b] ml	Init. DDT level, ppm	^{14}C recovered,[c] %	Mass ratio[d] *p,p'*-DDT: *p,p'*-DDD	Tlc zones[e] A:B:C
8	5 μCi, 0.075 mg	28	25	2.8	not measured	1:7.2	36:51:13
9	5 μCi, 10 mg	7	100	100	75	1:17	85:5:10
10	5 μCi, 10 mg	14	100	100	70	1:2	85:7.5:7.5
11	5 μCi, 10 mg	21	100	100	78	1:5.4	80:8:12
12[f]	5 μCi, 10 mg	28	100	100	72	1:2.1	58:26:16
13 (contr)	0,0	28	100	0	...	...	...
14 (contr)	0,0	14	100	0	...	...	...

[a] Incubations under hydrogen at 35°C.
[b] ca. 5% solids w/w.
[c,d,e] See notes *b, c, d,* Table I.
[f] Label in aqueous phase after incubation measured for experiment 12 <0.0011 μCi.

and the residue subjected to a series of continuous hot (56°C) Soxhlet extractions with redistilled AnalaR acetone (B. D. H. Chemicals Ltd.) until no further activity could be recovered (>20 hr). To test the efficiency of extraction, samples from preliminary incubations were divided into two parts, and one part was extracted by this method while the other was extracted using heptane:isopropanol (1:4) at 20°C (Rhead, 1971). The ec-glc of the total extract from each method proved identical. Extracts were dried (anhydrous sodium sulfate), the solvent evaporated, and final drying effected by benzene or toluene azeotrope distillation. Residues were taken up in hexane (redistilled B. D. H. Chemicals Ltd. Laboratory Reagent Grade, tested for purity by glc). When large sediment samples (ca. 700 grams) were extracted, a modified procedure based on that of Guenzi and Beard (1967) was employed.

Extracts were counted (Isotope Developments Ltd., Liquid Measuring Head 2022), examined by gas chromatography (Perkin-Elmer F11 Chromatograph with ^{63}Ni electron capture detector, on-column injection, 6 ft × 0.25 in. silanized glass column of 1.5% OV-17, 1.95% QF-1 mixed phase on Diatoport S, 80–100 mesh, column temperature 200°C isothermal, nitrogen carrier 75 ml/min) and subsequently by thin-layer chromatography (Kieselgel G or GF$_{254}$ with *n*-hexane, ethyl acetate, acetic acid, 15:1:0.01 (solvent system I) or *n*-hexane, ether, acetic acid, 1:4:0.1 (solvent system II) followed by autoradiography or radioscanning (Panax Radiochromatogram Scanner, Model RTLS-1A). For details of combined gc-ms, see Figure 1.

Results and Discussion

Glc examination of the total extract of the in situ DDT incubations revealed only two peaks not present in controls and corresponding in retention time exactly with those of authentic *p,p'*-DDT and *p,p'*-DDD (standards from Analabs Inc.), the latter being present as a minor component (Table I). Tlc (solvent system I) followed by radioscanning revealed only one radioactive zone, R_f 0.55, indicating that no extractable polar products of *p,p'*-DDT degradation had formed, and, taken with the glc data, that the only degradation which had occurred in the estuarine environment over 46 days was the formation of a small quantity of *p,p'*-DDD.

In contrast, laboratory incubations of *p,p'*-DDT in estuarine sediments at ca. 30 ppm (Table II) produced greater conversion of *p,p'*-DDT to *p,p'*-DDD. No other single glc peak not

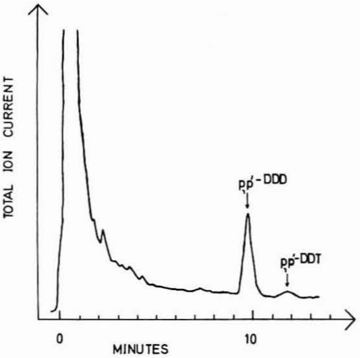

Figure 1. Application of gc-ms

Total ion current trace from gc-ms of total extract of *p,p'*-DDT incubation in Severn sediments under laboratory conditions (expt 5). Mass spectra were recorded using a Varian MAT CH-7 low-resolution mass spectrometer (Watson-Biemann separator) in conjunction with a Varian Aerograph 1200 gas chromatograph with a silanized stainless steel column, 8 ft × 1 mm i.d. of 1.5% OV-17, 1.95% QF-1 mixed phase on Diatoport S, 80–100 mesh, at 215°C; Helium carrier gas; 70 eV electron energy; 3 kV accelerating voltage.

present in the control was observed. However, the presence of certain DDT breakdown products to which the electron capture detector is relatively insensitive (Thompson et al., 1969) cannot be ruled out. Tlc analysis revealed the formation of small quantities of polar products (Table II, zones B and C) although the main radioactive zone occurred at R_f 0.45 with a shoulder at 0.54 corresponding to *p,p'*-DDD and *p,p'*-DDT, respectively (by tlc of standards and glc of the total extract tlc zones). The less than total recovery of label is not unexpected and is taken to indicate the progressively tighter binding of DDT and its breakdown products to clay minerals and cell debris with time (Fries et al., 1969). Recovery of label from sediments decreased as residence time increased. Tests for the evolution of $^{14}CO_2$ were conducted only in one experiment (expt 8) and proved negative (Guenzi and Beard, 1967). Glc and tlc data indicated that the major product of *p,p'*-DDT degradation in this system was *p,p'*-DDD, and this was confirmed by combined gas chromatography–mass spectrometry of the total extract (Figure 1) followed by comparison with the mass spectrum of authentic *p,p'*-DDD. Above *m/e* 100, mass spectra of authentic *p,p'*-DDD and breakdown products were identical and in agreement with published mass spectra (Biros and Walker, 1970). Below *m/e* 100, slight variations were noted between spectra, probably owing to other components in the total extract having the same gc retention time as *p,p'*-DDD.

When *p,p'*-DDT was incubated in sewage, considerably greater breakdown occurred (Table III). In expt 8, tlc zone A (including DDT and DDD) was no longer dominant, the more polar zone B accounting for 51% total recovered activity. Zone B gave one major peak on glc analysis, and it was thought this might correspond to DDNS (Matsumura et al., 1971). However, this was disproved following reduction of *p,p'*-DDT with zinc in HCl/HOAc which yielded two major components, identified by gc-ms as DDNS and DDMS [1-chloro-2,2-bis(*p*-chlorophenyl)ethane]. The extract of zone B gave a peak slightly longer in retention time than the latter reference compound.

Analysis of the polar zone C using tlc with solvent system II indicates the presence of a major zone R_f 0.13 to 0.30 (peak R_f 0.22) and a number of not completely resolved components, R_f range 0.37 to 0.80. Tlc data obtained using authentic *p,p'*-DDA [bis(*p*-chlorophenyl)acetic acid, Aldrich Chemical Co.] is consistent with the view that *p,p'*-DDA, R_f 0.48 is a component of this mixture although glc analysis following diazomethane treatment failed to confirm this. The ec detector is, however, 50 times less sensitive to this compound than to *p,p'*-DDT (Thompson et al., 1969).

The results of sewage incubations with 100 ppm *p,p'*-DDT are recorded in Table III, expt 9–12. No general trends are observable with incubation time under hydrogen, differences between experiments probably depending as much on variations between sewage samples as on the incubation time parameter. Glc analysis in all cases gave peaks not in controls and coinjecting with *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDMS, and *p,p'*-DBP (4,4'-dichlorobenzophenone). The formation of *p,p'*-DDD was confirmed by gc-ms of a total extract (expt 9). As in experiment 8, tlc zone B from experiment 12 gave one major glc peak and this, in the glc of the gross extract, formed a shoulder on the peak corresponding to *p,p'*-DDMS. In experiment 12, the mass ratio in the total extract of *p,p'*-DDT:*p,p'*-DDD was 1:2. The presence of *p,p'*-DDD in total sewage extract was confirmed by combined gc-ms Kelthane [1,1,1-trichloro-2-hydroxy-2,2-bis(*p*-chlorophenyl)ethane] is known to form DBP and other compounds on the glc column. The glc peak corresponding to DBP in the chromatogram of the total sewage incubation extract could thus be due either to Kelthane or DBP in the extract. To distinguish between these possibilities, the gross extract was treated with excess bis(trimethylsilyl)-trifluoroacetamide (BTSFA) which would derivatize any Kelthane present. On examination of the glc of the treated material, the DBP was found to have been unaffected and was therefore not derived from Kelthane.

Under the conditions used, we find *p,p'*-DDT degradation increasing in the sequence:

incubations in Severn mud in situ, 5–25°C < in Severn mud under H_2, 25°C < in anaerobic sewage sludge, under H_2, 35°C

Microbiological Studies

The microbiology of the Severn sediments was examined. The dilution plate count method was employed to estimate variations in the numbers of bacteria (Hawker et al., 1960; Skinner et al., 1952). Mud (10 grams) was shaken with sterile distilled water and serial dilutions were prepared in nutrient broth. Aliquots of the higher dilutions were mixed with cooled molten agar (45°C) in sterile Petri dishes, each sample being plated at least in duplicate. Two media selected for most dilution plate experiments were nutrient agar (Oxoid Blood Agar Base, No. 2) and a mud extract agar, chosen to resemble the estuarine sedimentary environment. Mud extract was prepared by mixing fresh estuarine mud (1 kg) with estuarine water (1 liter), autoclaving (15 min), filtering, making the resulting extract to 1 liter in estuarine water and autoclaving again. Agar (15 grams, Difco Bacto) and dipotassium hydrogen phosphate (0.5 gram) were added to mud extract (500 ml) and estuarine water was added to 1 liter. The whole was autoclaved (15 lb/in.^{2}) and glucose added to 0.1% w/v after separate sterilization immediately prior to use.

The counts of aerobic bacteria (yeasts and actinomycetes not estimated separately) were usually of the order of 10^6 to 10^7 organisms/gram of wet mud, while for anaerobically growing ones, this figure was of the order of 10^5 to 10^6/gram. A typical sample of surface mud (upper mobile silt excluding top one centimeter, collected 5/18/71) gave a count of 1.9 ×

10^7 aerobes and 3.5×10^6 anaerobes/gram wet mud, whereas lower mud (black mud, ca. 15 cm depth, collected 5/18/71) gave 5.7×10^4 aerobes and 4×10^4 anaerobes/gram wet mud (nutrient agar, 8-day incubations). The procedure used would probably fail to estimate large numbers of fastidious anaerobes. A mud sample which was actively evolving gas taken from the Bristol Avon River, a tributary of the Severn, gave counts of 1.5×10^7 aerobes and 1.1×10^7 anaerobes/gram wet mud following an identical experimental procedure. The percentages of chromatogens in most Severn estuary cultures were notably lower than in those from the Bristol Avon sample (Potter, 1964). Considerable variations in counts and colony types were frequently obtained pointing to the varied nature of the sedimentary environment at the sampling site (ZoBell and Anderson, 1936).

The effect of DDT on bacterial counts from the mud was investigated and it was found that DDT (mixed isomers) at 100 ppm in agar consistently reduced the overall count compared with controls. Typical results are given in Table IV. Kokke (1970) has shown that DDT included in culture agar at 0.1 ppm retarded or inhibited bacteria from ditch water and nursery soil. Ko and Lockwood (1968) have also demonstrated the inhibiting effect of DDT at 10 ppm on certain microorganisms although Lemire and Fredette (1961) have shown a stimulating effect on certain species of bacteria.

Bacteria isolated from estuarine mud were tested for their ability to degrade DDT in vitro. Results obtained to date indicate that many such bacteria are able to degrade DDT at least as far as DDD in broth culture, although a few are not able to bring about this transformation under these conditions. To test the degradation of DDT by bacteria in vitro, pure cultures were isolated from dilution plates containing DDT, purified by streaking several times on DDT agar, and inoculated singly into nutrient broth containing 10 ppm DDT. In some cases mixed cultures derived directly from the mud were inoculated. Controls consisted of nutrient broth alone and nutrient broth with 1% ethanol. Cultures were incubated in the dark at 20°C under normal aerobic conditions, but no precautions were taken to prevent the development of anaerobic conditions locally from the result of rapid bacterial growth in broth culture. After incubation, each culture was sonicated (5 min, Dawe Ultrasonic Agitator with Probe, Type 1130A) and then shaken with redistilled hexane and the extract examined by gas chromatography. The results of this investigation are set out in Table V.

Table IV. Effect of DDT on Bacteria in Vitro

Culture medium[a]	Plate counts[b] Aerobic, × 10^5	Plate counts[b] Anaerobic (under hydrogen), × 10^5
NA (Contr)	3.8	1.7
NA + EtOH (Contr)	3.0	1.9
NA + DDT	1.7	0.6
ME (Contr)	8.4	2.9
ME + EtOH (Contr)	5.6	2.4
ME + DDT	3.2	0.9

[a] NA = nutrient agar, ME = mud extract agar (see text), ME (or NA) + DDT = technical DDT (mixed isomers) in 1 ml EtOH added to 100 ml cooled agar to give 100 ppm DDT and the mixture added to sterile Petri dishes (20 ml/dish). ME (or NA) + EtOH control plates containing 1% v/v EtOH in medium. The reduction in plate counts shown here on addition of DDT is followed consistently in experiments using other media.

[b] Plate counts/gram wet mud, after 21-day incubation at 20°C.

Table V. Effect of Bacteria in Culture on DDT

(10 ppm DDT in nutrient broth)

Culture identification	Incubation time, days	Ratio DDD:DDT[a] in hexane extract
M6a[b]	7	1:5
D25XVI[b]	14	1:5
	14 (anaerobic)	1:12
M1 (gram −ve rod)	14	1:22
M2 (gram −ve rod)	14	1:40
M3	14	1:39
D5 (mixed culture)	37	1:1

[a] Mass ratio from glc peak area compared with standard mixture.

[b] Mixed isomers: p,p' and o,p isomers summed. Starting material o,p-DDT:p,p'-DDT, 0.11:1.00.

Many workers have tested the ability of microorganisms to degrade DDT in vitro, although most have used either known pure strains (Johnson et al., 1967) or a series of isolates from the natural environment, tested but not identified (Matsumura et al., 1971). Future work in this laboratory will follow Patil et al. (1970) and will involve both the identification of isolates and further tests on their ability to degrade pesticides, both in vitro and in situ in the estuary.

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Effect of Dissolved Salts on Water Solubility of Lindane

William L. Masterton[1] **and Tei Pei Lee**
Department of Chemistry, University of Connecticut, Storrs, Conn. 06268

■ The effect of 14 different 1:1 salts on the water solubility of lindane (γ-hexachlorocyclohexane) has been measured. In 10 cases, salting out is observed; the greatest decrease in solubility is found with the alkali fluorides, KF and NaF. The four electrolytes that salt in lindane [NaI, KI, $(CH_3)_4NCl$, $(C_2H_5)_4NCl$] are ones containing large ions. The order of the Setschenow parameters calculated from solubility data for lindane parallels that for benzene. Except for the fluorides, the extent of salting out is less for lindane than for benzene.

A recent review (Gunther et al., 1968) summarizes the available solubility data for pesticides in water. Neither there nor elsewhere in the literature does one find quantitative data for the effect of dissolved salts on pesticide solubilities. Yet it is well known that salts such as the alkali and alkaline earth halides can profoundly influence the solubility of simple organic compounds such as benzene. Most frequently, salting out—i.e., decreased solubility in the presence of salts—is observed; salting in (increased solubility) is less common.

Salt effect data for pesticides should be directly applicable to a variety of practical problems. In particular, they are necessary to estimate equilibrium concentrations of these species in marine and brackish waters. For these reasons among others, we have initiated a study of pesticide solubilities in aqueous salt solutions. Extensive measurements have been carried out with lindane (γ-hexachlorocyclohexane) using a variety of 1:1 salts. This compound was chosen because it is one of the simplest of the organic pesticide molecules and can be analyzed quantitatively even at very low concentrations by vapor phase chromatography with an electron capture detector.

Experimental

A sample of high-purity lindane (γ-isomer), furnished by the Hooker Chemical Corp., was recrystallized once from methanol to give a microcrystalline product. Its melting point was determined to be 113.2–113.4°C (lit. mp = 113°C). Heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-endomethanoindene), used as an internal standard for vpc measurements, was recrystallized several times from methanol until it gave a single peak on vpc analysis. Chromatographic grade *n*-hexane was used to extract samples from water solution for analysis. The salts employed were reagent grade, used without further purification except for $(CH_3)_4NCl$ and $(C_2H_5)_4NCl$, which were recrystallized from methanol.

To achieve saturation, 100-ml flasks containing about 0.05 gram of lindane and 50 ml of salt solution were immersed in a constant-temperature bath at 25.0° ± 0.05°C. The flasks were gently shaken mechanically for seven days; preliminary tests indicated that equilibrium was attained within five to seven days. The solutions were allowed to stand for at least 3 hr before sampling; after this time, no Tyndall effect could be observed. They were then transferred to stainless steel tubes and placed in an ultracentrifuge for 3 hr at 40,000 rpm to ensure removal of suspended particles. Analysis showed that solutions treated this way gave lindane concentrations only slightly lower than uncentrifuged samples. Longer centrifuging times and faster speeds did not change the observed lindane concentrations.

Five milliliters of the aqueous lindane solution was withdrawn with a pipet and extracted with 10 ml of hexane. Tests showed that a single extraction sufficed to remove at least 99.9% of the lindane. Five milliliters of an internal standard solution containing an appropriate amount of heptachlor in *n*-hexane was added to the extract. About 0.5 μl of the resulting solution was injected into a Hewlett-Packard Model 5750 Research Gas Chromatograph equipped with a high-temperature ^{63}Ni electron capture detector. The carrier gas was a mixture of 95% argon and 5% methane, with a flow rate of 20 ml/min. The column and detector temperatures were 200°

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[1] To whom correspondence should be addressed.

Table I. Effect of Dissolved Salts on the Water Solubility of Lindane at 25°C

	C_s	S_0/S		C_s	S_0/S		C_s	S_0/S
KF	0.249	1.37_7	NaBr	0.245	1.08_3	$(CH_3)_4NCl$	0.406	0.94_7
	0.499	1.88_9		0.490	1.17_5		0.608	0.92_4
	0.748	2.55_9		0.735	1.25_7			
	0.997	3.45_5		0.980	1.32_4			
NaF	0.251	1.29_2	RbCl	0.251	1.06_8	NaI	0.246	0.94_7
	0.502	1.63_5		0.503	1.13_9		0.493	0.89_7
	0.753	2.03_2		0.754	1.19_4		0.739	0.85_6
	1.004	2.59_3		1.005	1.27_9		0.985	0.82_8
NaCl	0.249	1.10_6	CsCl	0.247	1.04_2	KI	0.269	0.91_7
	0.498	1.22_8		0.494	1.09_6		0.538	0.86_6
	0.746	1.33_3		0.740	1.11_6		0.806	0.79_7
	0.995	1.44_6		0.987	1.16_8		1.075	0.72_3
KCl	0.245	1.09_3	NH_4Cl	0.412	1.06_8	$(C_2H_5)_4NCl$	0.403	0.83_6
	0.490	1.19_0		0.618	1.09_6		0.604	0.76_7
	0.735	1.27_9						
	0.980	1.39_8						
LiCl	0.248	1.08_4	KBr	0.245	1.02_2			
	0.496	1.17_1		0.490	1.04_4			
	0.744	1.25_3		0.735	1.07_4			
	0.992	1.36_3		0.980	1.10_6			

and 250°C, respectively. Single, sharp peaks were obtained for both lindane and heptachlor.

The areas of the two peaks were determined with a planimeter. The ratios of these areas were compared to those obtained with a series of 13 standard samples containing from 1.50 to 7.50 ppm of lindane in *n*-hexane to which the internal standard had been added. Response factors—i.e., ratios of areas of lindane to heptachlor peaks—for both the solution extracts and standard samples fell in the range 0.35–1.00. Over this range the concentration of lindane was a nearly linear function of the response factor, with a slight curvature at the upper end of the range.

The precision of the measurements was tested by repeated determinations of the solubility of lindane in pure water. The mean value obtained in 12 runs at 25.0°C was 7.52 ppm with a standard deviation of 0.041 ppm. In each solubility run with the various salts studied, one of the saturation flasks contained pure water. If the concentration of lindane found in that sample differed significantly from that determined previously, all of the data for the run were discarded.

With each of the alkali halides, lindane solubilities were determined at a series of four different salt concentrations ranging 0.25–1.0 mol/l. With NH_4Cl, $(CH_3)_4NCl$, and $(C_2H_5)_4NCl$, two different solutions were used, approximately 0.4 and 0.6*M*. Salt concentrations were ordinarily determined to ±0.1% by titrating a portion of the equilibrated solution for halide ion with silver nitrate using the Mohr method. Where this approach could not be applied, with sodium and potassium fluorides, the solutions were prepared to the desired molarity.

Results and Discussion

In Table I are listed the observed solubility ratios, S_0/S, where S_0 is the solubility (ppm) of lindane in pure water and S its solubility (ppm) in a salt solution of concentration C_s (mol/l.). Table II gives the Setschenow parameters, k_s, calculated by fitting solubility data to the equation

$$\log_{10} \frac{S_0}{S} = k_s C_s \qquad (1)$$

The best values of k_s were determined by least-squares analysis. The average deviation between the parameters listed in Table II and those calculated directly from the data in Table I at each salt concentration was ±0.005. The corresponding values of k_s for benzene are listed for comparison.

Of the 14 salts studied, 10 decrease the solubility of lindane in water ($k_s > 0$) while four increase its solubility ($k_s < 0$). The most obvious trend of the data in Table II is an increased tendency toward salting in with large cations and anions. The four salts that increase the solubility of lindane above that in pure water all contain either large cations, $(CH_3)_4^+$ and $(C_2H_5)_4N^+$, or the largest halide ion, I^-. Among salts of the

Table II. Setschenow Parameters for Lindane and Benzene[a]

Salt	k_s lindane (25°C)	k_s benzene
KF	+0.544	
NaF	+0.415	+0.254
NaCl	+0.166	+0.195
KCl	+0.149	+0.166
LiCl	+0.135	+0.141
NaBr	+0.131	+0.155
RbCl	+0.106	+0.140
CsCl	+0.069	+0.088
NH_4Cl	+0.066	+0.103
KBr	+0.043	+0.119
$(CH_3)_4NCl$	−0.057	
NaI	−0.088	+0.095
KI	−0.127	
$(C_2H_5)_4NCl$	−0.192	

[a] Values reported at 25°C by McDevit and Long (1952), except for NaF–benzene at 30°C by Saylor et al. (1952).

same metal with different halide ions, the Setschenow parameter invariably becomes algebraically smaller (less salting out or more salting in) as the size of the halide ion increases. Thus, for both sodium and potassium salts, k_s decreases in the order $F^- > Cl^- > Br^- > I^-$. This trend is less clear if one compares salts of different alkali metals containing a common anion. However, it is significant that the two alkali chlorides that salt out least are those with the largest cations, Rb^+ and Cs^+.

The salt orders for lindane and benzene are roughly parallel. With both nonelectrolytes, sodium fluoride salts out strongly while salts containing large ions—e.g., CsCl, NaI—either salt out less strongly or salt in. Salt effect data for benzene with tetraalkylammonium chlorides is not available. However, it is known (Bergen and Long, 1956; Desnoyers et al., 1965) that tetraalkylammonium bromides salt in benzene and that the magnitude of this effect increases with the chain length of the alkyl group. The Setschenow parameters for benzene with $(CH_3)_4NBr$, $(C_2H_5)_4NBr$, $(n\text{-}C_3H_7)_4NBr$, and $(n\text{-}C_4H_9)_4NBr$ at 25°C are −0.149, −0.248, −0.408, and −0.535, respectively. This same trend is evident with lindane where k_s increases in magnitude from $(CH_3)_4NCl$ ($k_s = -0.057$) to $(C_2H_5)_4NCl$ ($k_s = -0.192$).

With one notable exception, the Setschenow parameters for lindane with a given salt are algebraically smaller than those for benzene. In general, benzene is salted out to a greater extent than is lindane by a given salt at a particular concentration. The effect is particularly striking with sodium iodide, which salts out benzene ($k_s = +0.095$) but salts in lindane ($k_s = -0.088$). The one exception to this general rule among the 10 salts for which a comparison is possible is sodium fluoride, which salts out lindane more strongly than benzene (k_s lindane $= +0.415$, k_s benzene $= +0.254$). Salting out of lindane is even more extensive with potassium fluoride. Using Equation 1 with $k_s = +0.544$, one can calculate that in a $1M$ solution of potassium fluoride the solubility of lindane is less than one third of that in pure water.

It is of interest to compare the values of the Setschenow parameters observed for lindane with those predicted by various theories of the salt effect. Electrostatic theories (Debye and McAulay, 1925; Conway et al., 1964) relate the sign of k_s to the effect of the nonelectrolyte on the dielectric constant of water. Species which lower the dielectric constant should be salted out by all electrolytes. Clearly, electrostatic theory cannot explain why lindane is salted out by some 1:1 salts and salted in by others.

The internal pressure theory of the salt effect (McDevit and Long, 1952) attributes the sign of the Setschenow parameter to the influence that the salt has on the water structure. If it compresses the water structure, it becomes more difficult to introduce nonelectrolyte molecules, and k_s is a positive quantity. If the water structure is broken down by the addition of salt, the nonelectrolyte is expected to be more soluble, and k_s is negative. McDevit and Long derive the limiting equation for the Setschenow parameter:

$$k_s = \frac{V_i^o(V_s - \overline{V}_s^o)}{2.3\,RT\beta_0} \tag{2}$$

where V_i^o is the molar volume of the nonelectrolyte, V_s the molar volume of the (liquid) salt, $\overline{V}_s^o$ its partial molar volume in water at infinite dilution, R the gas law constant, T the absolute temperature, and β_0 the compressibility of pure water. The quantity $(V_s - \overline{V}_s^o)$, which may be either positive (salting out) or negative (salting in), is available for most of the salts used in this work. Except for the two iodide salts, the sign of k_s predicted by Equation 2 agrees with that found experimentally. Moreover, the salt order is approximately that predicted from the theory. However, Equation 2 further predicts that the magnitude of k_s for a given salt should increase with the molar volume of the nonelectrolyte. Comparing the molar volumes of lindane ($V_i^o = 150$ ml/mol) and benzene ($V_i^o = 89$ ml/mol), one would expect the Setschenow parameters for lindane to be considerably larger than those of benzene. Examination of Table II shows that the reverse is true. Of the 10 salts for which a comparison is possible, nine show values of k_s for lindane which are smaller than those for benzene.

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Energy Dispersive X-Ray Fluorescence Analysis of Air Particulates in Texas

John R. Rhodes,[1] Andrzej H. Pradzynski, and Colin B. Hunter
Columbia Scientific Industries, P.O. Box 6190, Austin, Tex. 78762

Jimmie S. Payne and James L. Lindgren
Texas State Department of Health, Air Pollution Control Services, Austin, Tex. 78751

■ Suspended particulate matter samples were collected in 38 Air Quality Control Network Stations in Texas using high-volume air samplers with 8 × 10 in. filter paper sheets, Whatman Type 41. Specimen discs 2 in. in diam were cut out from the sheets and measured in an automatic, energy dispersive X-ray fluorescence spectrometer using the radioisotope sources Fe-55, Pu-238, and Cd-109 for X-ray excitation. The following elements were determined: Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Hg, Pb, As, Br, Sr, Zr, and Mo. Standards made up from calibrated solutions deposited on filter paper and dried were measured along with the specimens and blanks. Analytical results were compared with those obtained by atomic absorption spectrophotometry. Air particulate pollution data from a statewide survey in Texas were compared with other available data. The method and equipment has proved itself capable of use for air particulate survey measurements and for pollution source location.

Environmental specialists are concerned not only with the total amount of particulates in the air but also with their chemical composition. Multielement analysis is necessary for revealing and identifying air particulate pollution sources. For routine, multielement analysis of large numbers of air particulate samples the analytical technique must be rapid and inexpensive. If such a technique were available, surveillance could be established over wide areas where air pollution is a problem.

Conventional analytical techniques such as gravimetry, colorimetry, emission spectroscopy, or atomic absorption spectrophotometry can generally provide the required sensitivity for the detection of metallic element air pollutants, but they are time- and labor-consuming. They require an experienced analyst to perform the determinations even when done routinely. They do not allow preservation of the sample for repeat analyses, since it must be dissolved. Furthermore, the necessary wet chemical sample preparation is an additional source of errors.

Emission spectroscopy (Morrow and Brief, 1971) and atomic absorption spectrophotometry (Thompson et al., 1970) are at present the most widely used methods in air pollution control laboratories. Emission spectroscopy is a multielement technique but requires careful sample pretreatment and is not considered to be very precise. Also, preparation of standards requires considerable care and effort.

Atomic absorption spectrophotometry is strictly a single-element analysis technique, but modern instruments have interchangeable lamps for sequential analysis of up to six elements per sample. A standardized 8 × 10 in. air particulate filter may not be large enough for sequential analyses of many elements, especially when the more accurate method of standard addition is used.

The sensitivities of both of these methods vary significantly from element to element. In fact, emission spectroscopy has insufficient sensitivity for such important potential pollutants as Se, Hg, As, Cd, and atomic absorption for As, Hg, Se.

Several papers have been published on the application of neutron activation for the analysis of air particulates—e.g., Dams et al., 1971; Brar et al., 1970; Zoller and Gordon, 1970. The method is very sensitive for some elements while quite insensitive for others—e.g., lead. To cover the whole range of elements of interest to air pollution control, access to a nuclear reactor is necessary and a long time between sample irradiation and measurement must be allowed [from several hours up to a few weeks for some elements, according to Dams et al. (1971)]. Neutron activation analysis can be used in special cases but is rather impractical for routine application.

X-ray fluorescence spectroscopy has been used for air particulate analysis by a few workers (Hirt et al., 1956; Bumsted, 1964). However, the conventional method, using a crystal spectrometer and sequential counting of each element has not found broad application in routine air particulate analysis. One reason could be the high capital cost and sophistication of the instrumentation.

The automatic, energy dispersive system with a Si(Li) detector and radioisotope sources, used in this work, has all the features required for routine, multielement air particulate analysis of large numbers of samples. No sample preparation is necessary, beyond cutting a 2-in.-diam piece out of the filter. The measurements are simultaneous for all the characteristic X-rays excited, and the method is nondestructive. Once loaded with samples, the apparatus can operate unattended.

Experimental

Sampling Procedure. The particulate samples obtained for this study were collected on 8 × 10 in. Whatman 41 filter paper. This was found to be essentially free of metallic elements whereas the standard glass fiber filters contain appreciable quantities of zinc, iron, barium, potassium, calcium, and strontium, rendering them quite unsuitable for the direct analysis methods used here. To eliminate errors due to hygroscopicity of the cellulose filters, they were stored for 24 hr in a constant-humidity box before each weighing, and weighed a fixed time (7 min) after removal from the box.

Two sets of samples were collected, the handling procedure being the same in each case. The filters were numbered, stored in the humidity box, weighed, and mailed to the sampling stations. The samples were collected on the specified day and the filters mailed back, stored in the constant-humidity box, reweighed and analyzed for 17 elements using the automatic energy dispersive X-ray spectrometer.

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[1] To whom correspondence should be addressed.

For comparison, 12 of the samples were also analyzed for six elements each by atomic absorption spectrophotometry.

The first set of 38 samples was collected on the same day in June 1971 at the stations indicated on the map of Texas in Figure 1. The second set of 51 samples was collected at one city, Corpus Christi, in three batches of 17 on three specified days in July 1971.

X-Ray Fluorescence Analysis. The analytical system used in this work is shown schematically in Figure 2 and consists of the following main components: automatic sample and source changer with capacities of 30 samples and four sources, respectively; three annular radioisotope source assemblies: Fe-55, 120 mCi: Pu-238, 400 mCi; and Cd-109, 12 mCi (Amersham Searle, Models IEC-K-259, PPC-5, and CUC-3, respectively); one 80 mm^2 $\times$ 4 mm thick Si(Li) detector and FET preamplifier with pulsed optical feedback, cooled by liquid nitrogen and having a resolution of 180 eV (FWHM) at 5.9 keV (Kevex Corp., Model 3000P); electronic circuitry detailed below; and a minicomputer (Nova with software supplied by Applied Computer Systems Division of Columbia Scientific Industries), with teletype terminal.

The electronic circuitry consisted of the following modules: high-voltage supply and amplifier with baseline restorer and pile-up rejector (Kevex Corp., Model 4000); spectrum stabilizer (Canberra Industries, Model 1520), set on a reference peak located at the high-energy end of the spectrum range; scaler with preset count (Mechtronics Nuclear, Model 701); analog to digital converter and 1024-channel analyzer with a scope display (Northern Scientific, Model NS-636). The baseline restorer with pile-up rejector is needed to preserve the spectrometer resolution at count rates above 1000 counts/sec (cps). However, the resultant high dead time causes the percentage of lost counts to vary significantly with the total detected count rate. These losses are not corrected for by the live time meter of the multichannel analyzer.

To provide accurate timing at high count rates, the peak from the reference source is monitored by the scaler. The accumulation of the X-ray spectrum in the multichannel analyzer is stopped by the scaler after a preset count is obtained in the reference peak. The radioisotope used in the reference source is Am-241 which has a half-life of 450 years.

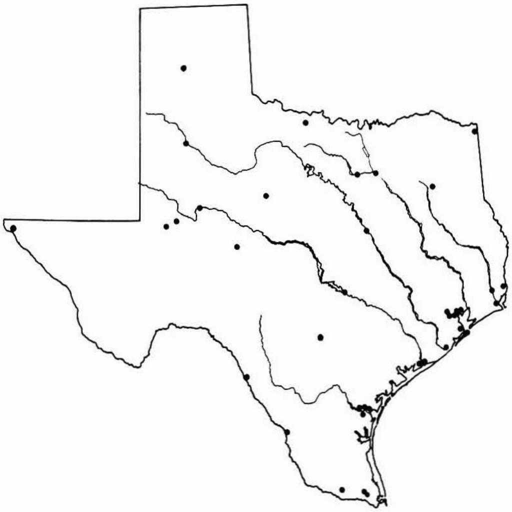

Figure 1. Locations of sampling stations in statewide survey

Method. Specimens in the form of discs of 47 mm diam were cut out of the original filter papers and measured in batches of 27 unknowns and three standards. To obtain the best excitation efficiencies, the 17 elements to be determined were divided into three groups, each excited with a different source, namely: Ca, Ti, V with Fe-55; Cr, Mn, Fe, Co, Ni, Cu, Zn with Pu-238; and Hg, Pb, As, Br, Sr, Zr, Mo with Cd-109. Each batch of specimens was counted with each of the three sources. The counting period was that required to accumulate 200,000 counts in the reference peak, which amounted to about 10 min/specimen with Pu-238 and Cd-109, and 5 min with Fe-55. A typical spectrum of an air particulate sample is shown in Figure 3.

The computer program was designed for automatic operation of the sample and source changer and the spectrometer system. Groups of channels were preset for K_α and K_β or L_α and L_β peaks of each element to be determined and for backgrounds between peaks. The data-processing part of the program was designed to integrate peak and background areas, subtract backgrounds from total peaks, subtract superimposed α- or β-peaks of adjacent elements using K_α/K_β and L_α/L_β ratios predetermined from multielement standards, and calculate element concentrations using calibration factors ob-

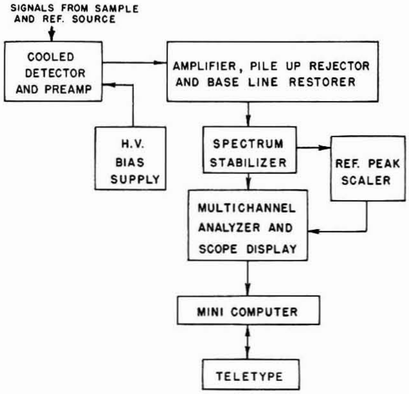

Figure 2. Schematic of radioisotope X-ray fluorescence analytical system

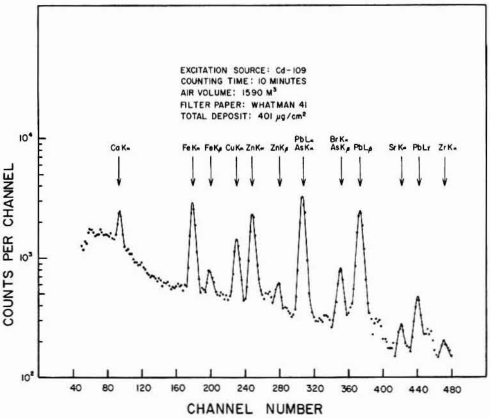

Figure 3. X-ray fluorescence spectrum of air particulate sample from west Texas

Table I. Selected Results of X-Ray

Location	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg
Amarillo	2.7	0.34	<0.006	0.01	0.05	1.5	<0.02	<0.01	0.12	0.15	<0.03
Beaumont	18.3	0.10	<0.011	0.06	0.04	0.4	<0.03	<0.02	0.23	0.01	0.05
Clute	29.9	0.22	<0.007	0.01	0.01	1.0	<0.02	<0.01	0.01	0.11	<0.03
Corpus Christi	21.9	0.29	<0.008	1.10	0.09	10.0	<0.02	<0.01	0.16	1.77	<0.03
El Paso	13.7	0.34	<0.008	<0.06	0.11	3.4	<0.02	<0.01	0.96	1.66	<0.03
Fort Worth	17.7	0.20	<0.008	<0.07	0.05	1.3	<0.02	<0.01	0.01	0.23	<0.03
Harlingen	11.8	0.20	<0.006	<0.05	<0.03	1.2	<0.02	<0.01	0.02	0.02	<0.03
Lubbock	8.5	1.33	<0.006	<0.05	0.17	8.6	0.05	<0.01	0.01	0.05	<0.03
Dallas	4.8	0.08	<0.004	0.01	0.01	0.7	<0.01	<0.01	0.02	0.01	<0.02
Houston	6.6	0.11	<0.008	0.05	<0.03	0.6	<0.03	<0.01	0.22	0.14	<0.03
Matagorda	0.8	0.04	<0.005	<0.04	<0.02	0.2	<0.01	<0.01	0.36	<0.005	0.03
San Antonio	3.5	0.12	<0.004	<0.04	<0.02	0.1	<0.01	<0.01	<0.01	0.07	<0.02

tained from the standards. Element concentrations were printed out in $\mu g/cm^2$ of filter paper and in $\mu g/m^3$ of air.

The method of analysis was based on the thin-specimen theory described in an earlier paper (Rhodes et al., 1971). This theory assumes that no interelement effects (enhancement and absorption) occur if the specimen obeys the thin-specimen criterion:

$$\mu m \leq 0.1$$

where μ is the sum of the mass absorption coefficients of the specimen for incident and fluorescent X-rays (cm^2/g), and m is the mass per unit area of the specimen (g/cm^2).

Compliance with the thin-specimen criterion was checked by a calculation of the average mass absorption coefficient of a mixture of 95% SiO_2 + 5% FeS for the X-ray energies of a Pu-238 source. The calculated critical specimen thickness is 1600 $\mu g/cm^2$ while the average thickness of real specimens collected in the first batch of particulate samples was 368 $\mu g/cm^2$.

STANDARDS. Since for thin specimens the characteristic X-ray intensity is a linear function of the concentration of the emitting element over a wide range of concentrations, we used in this work single calibration factors for each element. The calibration factors were calculated from multielement standards with concentrations of the main elements similar to those in real air particulate samples. Each standard contained 200 $\mu g/cm^2$ of Ca, 20 $\mu g/cm^2$ of Fe, 5 $\mu g/cm^2$ each of Pb and Br and 1 $\mu g/cm^2$ of three to five other elements. The elements present in one standard were selected to avoid spectral interferences. The standards were prepared from solutions containing mixtures of elements in the desirable concentrations, uniformly deposited on Whatman 41 filter paper discs, and were measured in strictly the same conditions as were the real specimens. Calibration factors were calculated in terms of cps/$\mu g/cm^2$ of element. Actual intensity ratios, K_α/K_β and L_α/L_β, were calculated from the standards for use in unfolding any α-β interferences in the real samples.

The quality of analytical results depends on the accuracy of standards used. An ideal standard would be a filter paper with a collected air particulate deposit analyzed by several independent laboratories using reliable methods of analysis (such as standard reference materials prepared by the NBS). This is, however, difficult to achieve since air particulate matter varies much in elemental composition (see Table I) and particle size distribution. We chose standards made up from solutions because this was the easiest way to obtain all the desired combinations of elements in the appropriate concentrations. However, work is in progress on preparation of particulate standards, to simulate natural samples more closely.

Atomic Absorption Analysis. As an independent check on our X-ray fluorescence results, several samples were analyzed by atomic absorption spectrophotometry, in a different laboratory by different personnel. Twelve arbitrarily chosen filters from the first set were analyzed for Cr, Mn, Fe, Ni, Cu, Zn, Pb, Cd, As. Preliminary experiments showed that the method of standard addition gave more accurate results than the external standard method. The following procedure for sample preparation was used: a 2-in. strip was removed from across the width of the filter. The strip was cut into small pieces and dissolved in 50 ml of concentrated nitric acid. After heating to provide for complete digestion of the cellulose, the sample was taken down to approximately 5–10-ml volume. Approximately 30 ml of distilled water was added and the sample then filtered through a quantitative filter into a 100-ml volumetric flask. The filter was washed with distilled water until the volumetric mark was reached.

Individual standard solutions were prepared containing known concentrations of each of the elements to be determined. Three multielement standards with increasing concentrations were prepared, each of which consisted of all the elements listed in Table I. Four 20-ml aliquots of each sample were placed in 25-ml volumetric flasks. The first flask of each sample was diluted to the mark with distilled water. Aliquots of the three complex standards were added to the remaining flasks so that each flask contained an equal amount of the sample plus increasing concentrations of the metal ions to be determined.

The solutions from each of these flasks were aspirated through the atomic absorption spectrophotometer (Bausch and Lomb, Model AC 2-20), under the optimum instrument conditions for each of the metals contained in the complex standards, and the observed absorbances were recorded. The absorbances obtained were plotted vs. the concentration of metal ion added to the sample aliquots. The actual concentration of the sample was then determined by back extrapolation of the Beer's law plot. Although the method of addition is very time-consuming, it is indispensable if the concentrations of trace quantities of metals in a complex matrix are to be determined accurately without significant matrix effects.

Results and Discussion

X-ray fluorescence analyses of the two sets of samples collected at different stations over the State of Texas (Figure 1) were expressed in terms of $\mu g/m^3$. Data from selected loca-

Fluorescence Analyses, $\mu g/m^3$

Pb	As	Br	Sr	Zr	Mo
0.32	<0.01	0.09	0.01	0.01	0.01
0.44	0.01	0.16	0.02	<0.01	0.02
0.60	<0.01	0.11	0.05	0.01	<0.007
0.80	0.01	0.07	0.04	<0.008	0.01
2.56	0.09	0.25	0.03	<0.008	0.02
0.54	<0.01	0.19	0.02	<0.008	0.01
0.04	<0.01	0.02	0.01	<0.006	<0.006
0.26	<0.01	0.08	0.04	0.05	<0.006
0.67	<0.01	0.24	0.01	<0.004	<0.004
1.03	<0.01	0.47	<0.01	<0.008	<0.008
0.04	<0.01	<0.03	<0.007	<0.005	<0.005
0.33	<0.01	0.10	<0.006	<0.004	0.10

tions are shown in Table I. The average concentrations and concentration ranges in both series of analyses are shown in Table II.

In Table III the values of arithmetic mean concentrations obtained in this work were compared with some of the few available data published. The data in Table III for U.S. average and for Gulf South average are biweekly averages for urban areas. Our data from the first series of measurements are from 24-hr sampling on a single day, in mostly urban areas. However, some of the sampling stations were not typically urban because of a very low density of population. As far as data obtained over such wide ranges of time, area, and sampling frequency can be compared, one must conclude that the orders of magnitude obtained in this work are in good agreement with the published data and some of the values are strikingly close.

Table IV compares atomic absorption with X-ray fluorescence data for several samples from the first series.

The detection limits of the two methods are compared in Table V. For X-ray fluorescence the detection limit was taken as three times the standard deviation of the background under each peak obtained in a 10-min count. The detection limit for atomic absorption was assumed equal to twice the standard deviation of 10 repeat measurements of the same specimen. It is seen that radioisotope X-ray fluorescence, as applied here, is at least as sensitive as atomic absorption for most of the elements compared. It can be seen from Table V that the X-ray fluorescence sensitivities for single elements vary from element to element, improving with increasing atomic number within the three groups measured using different excitation sources. The background subtraction routine also has some effect on the sensitivity of detection of single elements in computerized data processing. In this work the background was measured in three or four parts of the spectrum for each source and the baselines under individual peaks interpolated.

If necessary, there are several ways available to improve the sensitivity: increasing the number of channel groups for background determination, using a detector with a better resolution, and reducing the background by improved charge collection from the Si(Li) detector, according to Goulding et al. (1971). Still another way of improving the sensitivity is the use of the most efficient energies for X-ray excitation. This is easy for single element determinations but not for multielement analyses.

Since the Air Pollution Control authorities have not yet issued official guidelines for threshold limits of metallic element concentrations in air particulate matter, the detection limits for X-ray fluorescence were compared in Table V with the values adopted by the American Conference of Governmental Industrial Hygienists (ACGIH, 1971). It was assumed that concentrations of metallic elements in air particulate matter to be determined in air pollution control analyses are in the order of $^1/_{100}$ of the threshold limit values adopted by the ACGIH. An examination of columns 3 and 4 in Table V shows that the X-ray fluorescence detection limits are at least two orders of magnitude lower than $^1/_{100}$ of the ACGIH values. According to this criterion, therefore, the sensitivity of radioisotope, energy dispersive X-ray fluorescence analysis is more than sufficient for air particulate analysis of the quoted elements.

Another feature that needs to be discussed when introducing a new analytical method is precision of the results. It is believed that for the purpose of large area surveillance or

Table II. Concentrations of 17 Elements in Air Particulate Matter in Texas

($\mu g/m^3$)

	Statewide survey			Corpus Christi		
Element	Min.	Max.	Arithmetic av	Min.	Max.	Arithmetic av
Ca	0.6	29.9	7.73	0.80	12.4	5.14
Ti	0.02	1.33	0.19	0.02	0.41	0.11
V	<0.004	. . .	. . .	<0.004	0.05	. . .
Cr	<0.05	1.1	0.03	<0.05	0.50	. . .
Mn	<0.02	0.17	0.05	<0.02	0.08	. . .
Fe	0.1	10.0	1.3	0.20	3.10	0.68
Co	<0.018	0.05	<0.018	<0.018	0.02	. . .
Ni	<0.01	. . .	. . .	<0.013	0.01	. . .
Cu	<0.01	0.96	0.12	<0.011	0.07	0.03
Zn	<0.005	1.77	0.13	<0.006	4.28	0.21
Hg	<0.02	0.05	. . .	<0.02	0.06	. . .
As	<0.01	0.09	. . .	<0.022	0.04	. . .
Pb	0.02	2.56	0.36	<0.025	1.28	0.38
Br	0.02	0.47	0.10	0.01	0.53	0.15
Sr	<0.009	0.05	0.01	<0.009	0.17	0.01
Zr	<0.006	0.05	0.003	<0.006	0.02	. . .
Mo	<0.006	0.02	0.004	<0.006	0.18	. . .

source identification, a 10% level of precision is adequate. At high concentrations of analyzed elements, factors such as instrument stability, repeatability of sample handling, and sample homogeneity influence the precision. In a special reproducibility test, the instrumental drift of our system over one day was found to be less than 0.2%. Long-term stability, over the last year, is of the same order. At low concentrations, for example, below five times the detection limit, the main source of error is counting statistics. The various methods discussed for improving the sensitivity will equally well improve the precision at low concentrations.

An important factor in assessing the usefulness of an analytical technique is the time and labor requirement per specimen per element. The following estimates were made on the basis of experience from the present work. The times of analysis per specimen for 20 elements (in a batch of 100 specimens) for three methods compared were:

	Operator hr	Equipment hr
Atomic absorption (with external standard)	3	1
Atomic absorption (standard addition)	10	6
X-ray fluorescence (automated)	0.2	0.45

Table III. Comparison of Air Particulate Concentrations in Texas with Other Data

(Arithmetic av, $\mu g/m^3$)

	Tex. av (this work)	U.S. av (1960–65) (NAPCA, 1969)	Gulf South av 1958 (USPHS, 1966)	New York (1969/1970) (Morrow et al., 1971)
Ca	7.73	. . .	. . .	1.17
Ti	0.19	0.04	0.02	. . .
V	<0.10	0.05	0.12	0.17
Cr	0.03	0.015	0.025	. . .
Mn	0.05	0.10	0.07	. . .
Fe	1.30	1.58	1.30	2.98
Co	<0.02	<0.0005	. . .	. . .
Ni	<0.02	0.034	0.023	0.18
Cu	0.12	0.09	0.04	0.29
Zn	0.13	0.67	0.19	. . .
As	<0.03	0.02	. . .	. . .
Pb	0.36	0.79	0.40	1.37
Br	0.10	. . .	. . .	. . .
Sr	0.01	. . .	. . .	. . .
Zr	0.003	. . .	. . .	. . .
Mo	0.004	<0.005	0.02	. . .

Although the present survey was intended as a test of the technique rather than a search for pollution sources, two hitherto unknown sources were revealed, and several elements and element combinations were found to correlate with possible types of pollution. In this preliminary study the most interesting elements were Ca, Ti, Cr, Fe, Cu, Zn, Pb, As, Br, and Mo. The low values for V and Ni are noteworthy in view of their importance as pollutants in certain other locations. Mercury in particulate matter was generally undetectable.

Almost all the samples contained lead and bromine in amounts correlated with vehicular pollution. Lead/bromine ratios were generally up to a factor of two higher than the value of 2.56 expected from the 1 to 1 atomic ratio found in automobile engine combustion products. Since bromine tends to volatize, this is not unexpected. However, no Pb/Br ratios significantly smaller than 2.5 were found, indicating a low probability of independent bromine sources. Some ratios greater than 10 were found, indicating a strong probability of independent sources of lead. In one case, in the vicinity of a smelting plant, the high lead value was associated with high copper and zinc concentrations. Note that lead/bromine ratios can be measured directly and conveniently using X-ray fluorescence, whereas this is not the case with most other analytical techniques.

Other elemental associations, such as chromium and zinc, were also found to be correlated with emissions from certain metallurgical plants. Although ubiquitous, iron was found to offer possibilities of tracing steel plant emissions.

Further Work

There are several sources of inaccuracy in radioisotope X-ray fluorescence analysis that we are currently investigating.

Finite particle size of the air particulate sample reduces the characteristic X-ray intensity compared with a homogeneous layer (Berry et al., 1969). Work is being performed by our group to fully investigate the nature of the particle size effect and to reduce it. The results obtained will be published elsewhere (Rhodes, 1972). Assuming that our specimens are

Table IV. Comparison of Results of X-Ray Fluorescence and Atomic Absorption Analyses

	Mn		Fe		Cu		Zn		Pb	
	AA	X-ray	AA	X-ray	AA	X-ray	AA	X-ray	AA	X-ray
Amarillo	0.02	0.05	1.48	1.5	0.10	0.12	0.20	0.15	0.35	0.32
Beaumont	0.03	0.04	0.65	0.4	0.13	0.23	0.11	0.01	0.46	0.44
Clute	0.03	0.01	0.98	1.0	0.03	0.01	0.13	0.11	0.55	0.60
Corpus Christi	0.08	0.09	4.41^a	10.0	0.16	0.6	1.37^a	1.77	0.75	0.80
El Paso	0.10	0.11	2.61	3.4	0.89	0.96	1.55^a	1.66	2.73	2.56
Fort Worth	0.05	0.05	1.53	1.3	0.01	0.01	0.69^a	0.23	0.66	0.54
Harlingen	0.02	<0.03	1.24	1.2	0.02	0.02	0.20	0.02	0.12	0.04
Lubbock	0.16	0.17	2.59	8.6	0.03	0.01	0.22^a	0.05	0.34	0.26
Dallas	0.01	0.01	0.75	0.7	0.02	0.02	0.10	0.01	0.66	0.67
Houston	0.02	<0.03	0.65	0.6	0.22	0.22	0.19	0.14	0.92	1.03
Matagorda	NA	<0.02	0.28	0.2	0.31	0.36	0.37^a	<0.005	0.08	0.04
San Antonio	0.01	<0.02	0.62	0.1	0.06	<0.01	0.51^a	0.07	0.46	0.33

[a] Burner was readjusted because of high absorbances.

monolayers (such an assumption is justified by a simple calculation: a monolayer of spheres of 2.0 μ diam and of 3.0 g/cm^3 density would have a mass per unit area 360 μg/cm^2, which is very close to the average 368 μg/cm^2 of the samples analyzed in this work), this effect for the size range of air particulate matter—i.e., 0.1–10.0 μ and for the quoted elements causes a difference in intensities of less than 10% compared to standards made from solutions. The effect increases with increasing particle size (in 1–10-μ range) and with decreasing atomic number. Simplified mathematical expressions have been derived that can be introduced as correction factors. Also the use of standards prepared from powders of the same particle size distribution as the real samples would minimize the effect. Preparation of such standards is under way.

In a few regions of the spectrum, overlapping lines from different elements cause errors which are unlikely to be eliminated by improvement in spectrometer resolution. In some cases the peaks are not even resolved by conventional crystal spectrometers. We aim to investigate alternative approaches to these problems, such as spectrum unfolding and stripping techniques, which can be performed very quickly on a minicomputer without significant increase in computing power.

It is also our goal to extend the number of elements determined to include certain other important elements such as Cd and Ba. This would involve reappraising the choice of excitation sources.

We conclude from this work that automated, radioisotope X-ray fluorescence analysis using a Si(Li) spectrometer has proved itself capable of use for air particulate survey measurements and for pollution source location.

Table V. Detection Limits Compared with Threshold Limits

	X-ray fluorescence			Atomic absorption		1/100 of threshold limit values,
Element	Source	μg/cm^2	μg/m^3 [a]	μg/cm^2	μg/m^3 [a]	μg/m^3
Ca	Fe-55	0.06	0.013			
Ti		0.05	0.011			
V		0.03	0.007			1
Cr	Pu-238	0.24	0.053	1.42	0.40	5
Mn		0.12	0.027	0.20	0.056	50
Fe		0.08	0.018	0.54	0.118	100
Co		0.08	0.018			1
Ni		0.06	0.013			10
Cu		0.05	0.011	0.26	0.072	1
Zn		0.03	0.006	0.038	0.010	50
Pb		0.11	0.025	0.52	0.14	1.5
As	Cd-109	0.10	0.022	2.27	0.50	5
Br		0.18	0.040			7
Sr		0.04	0.009			
Zr		0.03	0.006			
Mo		0.03	0.006			50

[a] Conversion of μg/cm^2 into μg/m^3 has been done assuming an average filter area of 420 cm^2 and an average air volume 1880 m^3.

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NOTES

Nerve Gas—Isopropyl Methylphosphonofluoridate (GB)—Decomposition and Hydrostatic Pressure on the Ocean Floor

W. A. Adams

Inland Waters Directorate, Department of the Environment, Ottawa, Ont., Canada

■ The half-life of the hydrolysis of isopropyl methylphosphonofluoridate (GB) is estimated to increase by 25% at a depth of 4000 meters and 69% at a depth of 10,000 meters.

In his article, "Rate of Decomposition of GB in Seawater," (Epstein, 1970), did not comment on the effects of hydrostatic pressure on the rate of hydrolysis of isopropyl methylphosphonofluoridate (GB). Since the pressure generated by seawater is approximately 1 bar (0.987 atm)/10-meter depth and the average overall depth of the world's oceans is 4×10^3 meters, the pressure environment of GB leaking from disposal containers after deep-sea burial is 0.4 kbar.

Considering the same three hydrolysis reactions as Epstein that remove the fluoride from GB to make it biologically harmless [reactions with: (a), $MgOH^+$, rate constant k_2; (b), $CaOH^+$, rate constant k_2'; and (c), OH^-, rate constant k_2''] and the three hydrolysis equilibria associated with the hydroxide reactants involved [(a) K_a, (b) K_a', and (c) K_w], the effect of pressure on the overall first-order rate of decomposition was estimated in this work. Partial molal volumes of the species involved in the hydrolysis equilibria were used to calculate the overall volume changes, $\Delta\bar{V}^o$, associated with K_a (+25 cm³ mol⁻¹), with K_a' (+9 cm³ mol⁻¹), and with K_w (−20 cm³ mol⁻¹). Assuming that the alkaline hydrolysis reactions of GB are similar to the alkaline hydrolysis of esters and amides (Laidler and Chen, 1958) and considering the linear correlation found between the entropy of activation, $\Delta S\ddagger$, and the volume of activation, $\Delta V\ddagger$, (Laidler and Chen, 1959), a volume of activation of -12 cm³ mol⁻¹ was adopted as a value that fitted the $\Delta S\ddagger$, of -24 e.u. found experimentally for the hydrolysis of GB (Larsson, 1957). Equilibrium constants (and the reaction rate constants) are related to pressure by the following equation first discussed by Planck (1887).

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = \frac{-\Delta V}{RT} \qquad (1)$$

Equation 1 indicates that at 1 kbar for a ΔV of +20 cm³ mol⁻¹, the ratio K (1 kbar)/K (1 atm) is 0.45 while for a ΔV of −20 cm³ mol⁻¹, the ratio K (1 kbar)/K (1 atm) is 2.24.

The equilibrium constants and rate constants adjusted to 0.4 kbar are substituted into Equation 2 quoted by Epstein (1970), for the overall first-order rate constant for the decomposition of GB at a constant pH of 7.7. The first-order rate of decomposition, k, for constant pH, was expressed by Epstein as follows:

$$k = k_2 \cdot \frac{K_a \cdot C_o}{[H^+] + K_a} + k_2' \cdot \frac{K_a' \cdot C_o'}{[H^+] + K_a'} + k_2'' \cdot \frac{K_w}{[H^+]} \qquad (2)$$

where C_o and C_o' are the activities of Mg^{2+} and Ca^{2+} respectively in seawater. The pH decreases with depth in the ocean by approximately 0.02 pH units/1000 meters (Skirrow, 1965) and so this effect was neglected as was the effect of pressure on volume concentrations for this zero-order calculation. For 0.4 kbar and 25°C, the value obtained for the reaction half-life is 65 min. At 1 kbar pressure (equivalent to 10,000 meters depth), the half-life is 88 min. The half-life is 52 min (Epstein, 1970) at 1 atm pressure, which indicates an increase in half-life of 25% at 4000 meters depth and 69% at 10,000 meters depth.

The uncertainty in the pressure estimate is admittedly large (and hard to estimate), but the order of magnitude and sign of the effect is certainly not in doubt. It is not safe to ignore the hydrostatic pressure when the disposal of such toxic chemicals in the ocean depths is contemplated. A second pressure effect of interest when assessing risk is that the rate of diffusion of chemicals in aqueous systems under high pressure is greater (up to 1–2 kbar, and from 0 to ~30°C) than at atmospheric pressure. This is a factor that will influence the concentration gradient of GB in the proximity of a leaking container on the ocean floor. On the subject of pressure effects on chemical reactions and equilibria, a good foundation has been begun experimentally and theoretically on many systems, so that rough estimates can be made of the modified behavior caused by high pressures (Hamann, 1963). Unfortunately there is little data available on the effects of pressure on diffusion (Barton and Speedy, 1970; Horne, 1969). The importance of these considerations is worth emphasizing with respect to underground nuclear tests and deep-well disposal practices, since the fate of radioactive and/or toxic material released into the sea or groundwater deep in the earth is dependent on the high pressures found in these environments.

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Size Distribution of Suspended Particles from Lignite Combustion

Robert E. Lee, Jr.[1] **and C. Frederick Smith**

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

■ Particle size distribution measurements in Ankara, Turkey, which relies heavily on high-volatile content lignite fuel, reveal an average particle size predominantly greater than 1 μ in diam. Compared to the submicron-sized aerosols found in urban air in the U.S. and Britain, total suspended particulate matter in Ankara presents less of an inhalation hazard for equivalent concentrations.

Information on the particle size distribution of suspended particulate matter in air is very meager, mainly because suitable measuring devices have only recently become available. Modification of a commercially available impactor to operate at a sampling rate of 5 ft^3/min in conjunction with micro weighing techniques has permitted the estimation of size distributions of suspended particles in air on a gravimetric basis (Lee and Flesch, 1969; Lee and Goranson, 1971). Size measurements of ambient aerosols using the modified impactor are made on a regularly scheduled basis in eight urban and two nonurban areas in the U.S. (Lee and Goranson, 1971), in special studies in Great Britain (Lee et al., 1971), and at other sites in the U.S. The particle size distribution data collected in previous studies clearly indicate the predominantly submicron size of suspended particulate matter in air.

A major source of aerosols in urban air is the incomplete combustion of fuels including petroleum derivatives such as heating oil, natural gas, and gasoline; and the combustion of high grade and preprocessed coal. Fuels of these types are generally burned efficiently without excessive visible emissions. However, there are some areas in the world which must rely on lignite, a low-heat coal, as the principal source of fuel.

The particle size distribution of aerosols emitted from the combustion of fuels having a high volatile content has not been previously determined. The fraction of the aerosol which remains suspended in air after the inefficient combustion of poor-quality fuel can have an important bearing in assessing the respiratory health hazard and other pollution effects such as visibility reduction, soiling, and particle-gas interactions.

During a recent air-monitoring study in Ankara, Turkey, we made some particle size distribution measurements. This urban area relies heavily on low-quality, highly volatile lignite coal for fuel. About 612,000 metric tons of low-heat-value lignite coal (calorific value of 2500–3500 kcal/kg, 30% water, 20% ash, and 3–4% sulfur) are combusted annually in Ankara and account for an estimated 65–70% of the particulate emissions, primarily from residential heating (TBTAK, 1970). Ankara, with a population of slightly over one million inhabitants, is surrounded by hills about 1100 meters high; the center of the city is only about 850 meters high. The ditch-like geographical configuration of the city, in conjunction with little wind motion (average wind speed is only 2–3 meters/sec), contribute to the formation of frequent temperature inversions which prevent the dispersal of suspended particulate matter and other pollutants.

Ten 24-hr samples were collected during April and May 1971 with the NASN cascade impactor (Lee and Flesch, 1969) near the center of Ankara at the Hygiene School. Samples were collected at the second floor level to minimize collection of reentrained particles from the ground. The size distribution of the fractionated particulate matter, expressed as equivalent spheres of unit density, was determined gravimetrically after being conditioned for 24 hr in a constant temperature-humidity-controlled room. The composited data are plotted as log-normal distributions in Figure 1; the concentrations and various size parameters for each sample are given in Table I. Table I shows that the mass median diameter (MMD) of particles in Ankara air ranged from 1.21 to 2.19 μ with an average MMD of 1.79 μ composited by impactor stage for the 10 samples. These data indicate that suspended particulate matter in Ankara air is distributed in sizes predominantly greater than 1 μ. In contrast, samples collected from April–June 1970 in Cincinnati and Philadelphia had average MMD's of 0.54 μ and 0.26 μ, respectively (Lee and Goranson, 1971); seven samples collected in London during May 1970 had an average MMD of 0.66 (Lee et al., 1971). Figure 1 gives a comparison of the size distribution of samples collected during an equivalent season in other cities. Aerosols from these urban sites, which are typical of those found throughout the U.S. and Britain, illustrate the predominantly submicron particle size. These areas use fuel with a high heating quality in contrast to the fuel used in Ankara.

The range of particle sizes (aerosol dispersion) in Ankara air, as measured by the geometric standard deviation, is broad; similar dispersions are found in U.S. and British urban air. It is likely that a broad particle dispersion is predominantly due to the age of the emission aerosol and/or the

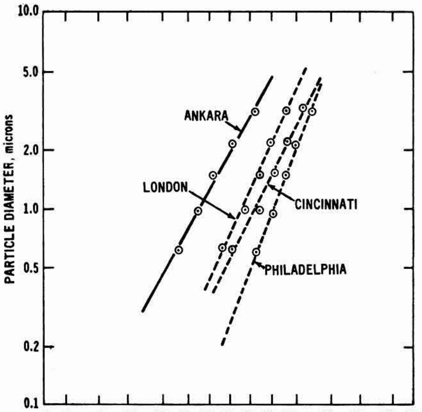

Figure 1. Composite particle size distribution curves

(a) Ankara, 10 samples collected from 4-26-71 to 5-5-71; (b) London, 7 samples collected 5-70; (c) Cincinnati, 6 samples collected from 4-70 to 6-70; and (d) Philadelphia, 7 samples collected from 4-70 to 6-70

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[1] To whom correspondence should be addressed.

coagulative activities which yield large particles by growth processes from smaller particles, however other factors may have an influence. With emission aerosols in Ankara, large newly formed particles are injected into the air from the incomplete combustion of lignite fuel, whereas the smaller particles with a lower settling velocity have a comparatively longer residence time. Further, the almost continuous inversion conditions which exist in Ankara can also contribute to a wide range of particle sizes by growth processes.

Comparisons of the particle size distribution of suspended particulate matter in Ankara with urban areas in the U.S. and Great Britain reveal the uniqueness of the aerosol in Ankara air. The large average particle size appears to be characteristic of aerosols emitted from the combustion of poor-quality lignite fuels since this is the only major difference between Ankara and the other urban areas sampled. Although the aerosol concentration in Ankara is higher than those found at the U.S. and British urban sites, the respirable fraction is low for equivalent concentrations. Hatch and Gross (1964) concluded that the percentage penetration of particles into the pulmonary air spaces rises from essentially zero at 10 μ to a maximum at and below about 1 μ. An average aerosol in Ankara less than or equal to 1 μ diam is 37% while, by comparison, the average yearly values for 1970 in six U.S. cities (Chicago, Cincinnati, Philadelphia, St. Louis, Washington, D.C., and Denver) ranged from 54 to 68% (Lee and Goranson, 1971). Further measurements need to be made to characterize the chemical composition of the various size fractions in urban areas which use low-quality fuel, especially in view of the possible presence of polynuclear hydrocarbons. However, the results reported here indicate that the inhalation hazard of the total particulate matter may not be as great as equivalent concentrations in U.S. and British cities.

Table I. Particle Size Distribution Parameters Measured in Ankara Air

Date	Concn, $\mu g/m^3$	MMD, μ	Geometric std dev	% Part. $\leq 1 \mu$	% Part. $\leq 2 \mu$
4-26-71	104.2	1.44	7.00	43	57
4-27-71	119.2	1.64	5.79	39	55
4-28-71	107.9	1.21	6.38	46	61
4-29-71	104.8	2.09	5.24	33	49
4-30-71	68.4	1.33	6.32	44	59
5-1-71	90.8	1.82	5.14	36	53
5-2-71	121.3	1.99	5.21	34	51
5-3-71	132.8	1.79	4.19	35	54
5-4-71	163.0	2.19	4.61	31	48
5-5-71	146.5	2.03	4.25	32	50
Composite	115.9	1.79	5.20	37	53

Acknowledgment

The authors thank Marilyn Hawkins for performing the gravimetric analysis and Stephen Goranson for the computer services.

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Determination of Bis-Chloromethyl Ether at the Ppb Level in Air Samples by High-Resolution Mass Spectroscopy

Ledelle Collier

Rohm and Haas Co., 5000 Richmond St., Philadelphia, Pa. 19137

■ Bis-chloromethyl ether vapor has recently been shown to be extremely toxic. A high-resolution mass spectral procedure with the capability of measuring bis-chloromethyl ether at the 0.1-ppb level in air containing other organic compounds has been developed. This procedure utilizes an enriching adsorber of Porapak Q, a high-surface-area aromatic copolymer in bead form, to adsorb the organic compounds from a volume of air. The adsorbed compounds are then thermally eluted into the reservoir of the mass spectrometer. The intensity of the ions at *m/e* 78.9950 ($ClCH_2—O—CH_2^+—$) is measured with a resolution of 1/3500.

Chloromethyl ether (CME, $CH_3—O—CH_2Cl$) is a commercial chloromethylating reagent widely used in the production of anion exchange resins, membranes, and other aromatic products. Typically CME contains several percent of bis-chloromethyl ether (BCME, $CH_2Cl—O—CH_2Cl$) as an impurity. Laskin et al. (1971) have shown that vapor samples of BCME are extremely toxic. Recent results (Collier, 1971) in our laboratory have shown that BCME is stable at 10 and 100 ppm in 70% r.h. air for at least 18 hr. CME hydrolyzes rapidly under similar conditions. An extremely selective method for the determination of BCME at the ppb level in air samples utilizing high-resolution mass spectroscopy will be reported.

The mass spectrum consists chiefly of ions produced by two distinct bond cleavages. These cleavages are $ClCH_2{+}O{-}CH_2Cl$ and $ClCH_2{-}O{-}CH_2{+}Cl$. The diagnostic ions are observed at *m/e*'s 49 and 51, and 79 and 81 (produced in pairs because of the ^{35}Cl and ^{37}Cl isotope ratio), respectively. The *m/e* 79 is the most abundant ion in the spectrum, thus making it the most sensitive choice for detecting BCME at very low levels.

The mass spectrometer is not sufficiently sensitive to detect BCME at the levels desired via direct introduction of an air sample. We therefore sought a means of concentrating the BCME by a factor of about 15,000. Porapak Q (Waters Associates, Inc., Framingham, Mass.) proved an ideal adsorber because water is not collected, BCME is efficiently adsorbed, and BCME is readily recovered from the column by thermal elution. Other advantages of porous polymer adsorbents have been cited (Williams and Umstead, 1968; Dravnieks et al., 1971).

Porapak Q has a high affinity for many organic compounds in air. Some of these compounds may produce ions at *m/e* 79 and/or *m/e* 81. The additional ions at *m/e* 79 and 81 consequently prevent the use of these peaks for measuring the quantities of BCME collected. High-resolution mass spectroscopy of the *m/e* 79 and *m/e* 81 peaks separates the diagnostic ions from the other ions, thus making it possible to make an accurate measurement for BCME.

Experimental

Enriching Columns. The enriching columns are 7-cm lengths of 5 mm o.d. glass tubing filled with 170 mg of Porapak Q 80/100 mesh resin. The ends of the glass tubes are partially constricted and packed with approximately 0.5-cm plugs of Pyrex wool to retain the beads. Before the beads are placed into the glass columns, they are cleaned by extracting with ethylene dichloride (EDC) in a Soxhlet extractor for a period of at least 6 hr at a rate of 6 cycles/hr. After the extraction is complete, the excess EDC is removed from the surface of the beads by placing them in a large beaker and flowing a gentle nitrogen stream over them with periodic stirring. After the glass columns are packed with the partially dried beads, they are heated at 200°C in a glass-lined vacuum oven for 2 hr under a pressure of <0.1 mm Hg. The ends of the adsorbers are then capped with rubber septums and the tube is stored in a screw cap jar until used.

Collection of Organic Vapors from the Atmosphere. The organic vapors are collected from the atmosphere by forcing 15 liters of air through an adsorber with an electric-powered Teflon-lined vacuum pressure pump at a rate of 1.5 l./min.

The sample size is measured using a calibrated rotameter in the line just before the adsorber. Experimentally, the adsorbers have been found to quantitatively adsorb BCME from 20 liters of air when the flow rate through them is 1.5 l./min or less. Routine samples do not exceed 15 liters in order to maintain a 5-liter safety margin.

The adsorber with the collected vapors is then capped at both ends with small rubber caps and stored until analyzed. Experiments have shown that the prepared samples are stable for over 18 days.

Mass Spectrometric Measurement

Standardization and Calibration of Instrument. The instrument used is a Hitachi RMU-6D double focus instrument, equipped with a 16-stage electron multiplier, and a heated all-glass-lined sampling system operated under the following conditions:

Mass range	0–300
Electron energy	70 eV
Acceleration voltage	3600 V
Electron current	75 μA
Ion source temp	200°C

When properly aligned, the instrument can easily be adjusted to a resolving power of approximately 1/3500 with the α and β slit widths set at 1.0 mm and the exit and collector slit widths at 0.150 mm. The slit widths are easily reproduced, thus making it possible to readily change the resolving power of the instrument.

To calibrate and standardize the *m/e* 78.9950 response for BCME, a liquid injection port is attached to the liquid-solid inlet and 1.0 μl of a solution containing 10.0 μg of BCME in EDC is injected. The vapors are collected in a gas reservoir, and after the liquid has completely vaporized and equilibrated, the valve between the reservoir and ion source is opened and a low-resolution spectrum of the mixture is obtained. The ion pattern in the low resolution spectrum is used to locate and set the instrument on the *m/e* 79 peak. Once the instrument has been locked on the *m/e* 79 peak, the resolving power is increased to 1/3500 by closing the exit and collector slits to 0.150 mm. The region *m/e* 78.9–79.1 is scanned, and the peak height at 78.9950 is measured. If we assume that a 5-mm peak can be measured, the detectable limit for this procedure is 0.1 ppb.

Analysis of the Prepared Adsorber for BCME. The adsorber is attached to the mass spectrometer liquid-solid inlet system using a detachable liquid-solid sample bulb. The air is pumped from the system while keeping the adsorber at room temperature. Once the system has been evacuated to less than 10^{-5} mm Hg, the line to the pump is closed, thus forming a reservoir for collecting the vapors from the column. The BCME and other adsorbed compounds are thermally eluted from the adsorber by heating at 180°C for 5 min. At the end of the 5-min period the valve to the analyzer is opened and the *m/e* 78.9–79.1 region is scanned. The BCME peak at *m/e* 78.9950 is measured and the ppb BCME calculated.

Quantitative recovery of BCME from the adsorber is obtained. This has been shown by injecting the same quantity of BCME directly into the mass spectrometer and comparing the height of the *m/e* 78.9950 peak obtained in this manner with the peak height obtained when the measured quantity of BCME is first injected into a 15-l volume of air, enriched with the adsorber and then analyzed. The peak heights obtained were found to be independent of the procedure.

Figure 1 shows the low-resolution spectrum of a typical air sample containing 2 ppb BCME. The *m/e* 78.9–79.1 region of the same spectrum under high resolution and the *m/e* 78.9–79.1 region in the spectrum of a standard BCME solution are shown in Figure 2.

Table I. Common *m/e* 79 Ions

(McLafferty, 1963)

Formula	Mass	ΔM	Resolving power
CH_4SiCl	78.9671	-0.0279	1/2800
CH_3S_2	78.9676	-0.0274	1/2800
C_2HClF	78.9751	-0.0199	1/4000
CH_4O_2P	78.9949	-0.0001	1/790,000
C_2H_4OCl	78.9950	0.0000	
C_5H_5N	79.0422	0.0472	1/1700
C_6H_7	79.0547	0.0597	1/1400

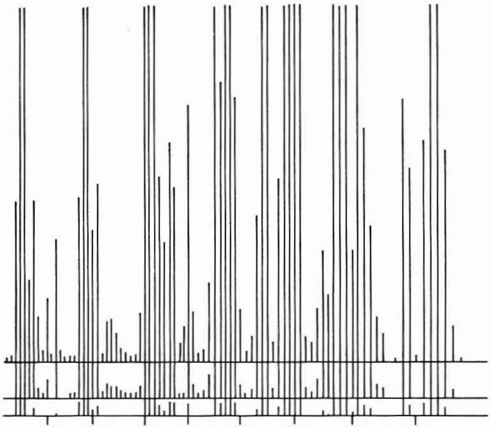

Figure 1. Low-resolution mass spectrum of typical air sample containing 2 ppb BCME

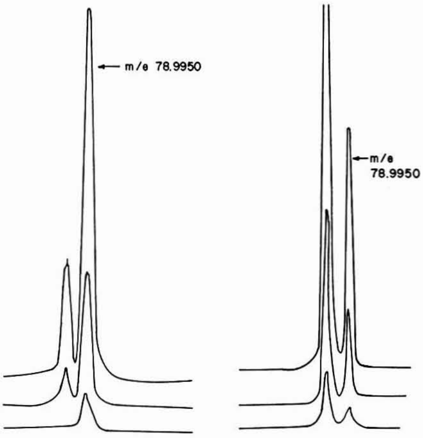

Figure 2. High-resolution spectrum around m/e 79 of standard BCME solution (left); high-resolution spectrum around m/e 79 of contaminated air sample shown in Figure 1 (right)

Discussion

Interferences encountered with low-resolution mass spectrometry and other techniques are virtually eliminated by this high-resolution technique. A list of ions appearing at m/e 79 is included as Table I. There are only two ions included in the list that a resolving power of 1/3500 is insufficient to distinguish completely, namely C_2HClF and CH_4O_2P. The C_2HClF ion, m/e 78.9751, might pose a slight problem in the absence of BCME for it appears very close to the same position as BCME and it is also a chlorinated fragment, thus, producing a peak at m/e 80.9722, $C_2H^{37}ClF$, which would present the same degree of interference to the m/e 80.9921, $C_2H_4O^{37}Cl$, peak from BCME. To determine whether an unknown ion at m/e 79 is C_2H_4OCl or C_2HClF, a small quantity of BCME can be added and the obtained spectra examined to see if the BCME peak and the unknown peak are identical or not.

The other ion that would pose a problem, if present, is CH_4O_2P, m/e 78.9949. To resolve this ion from the m/e 78.9950 ion in BCME requires a resolving power of 1/790,000 which is an impossibility. Since this is a nonchlorinated ion it is easily distinguished from the m/e 78.9950 ion from BCME by the absence of the 80.9921 ion, C_2H_4OCl.

The experience that has been obtained with this technique has shown it to be accurate and reliable. The combination of concentration of air pollutants on appropriate adsorbents followed by thermal elution and high-resolution mass spectrometric analysis should have broad applicability. The technique should certainly be considered whenever it is essential to monitor low levels of organic contaminants in air.

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Photosulfoxidation of Hydrocarbons in the Liquid Phase

Peter W. Jones[1] and Albert H. Adelman

Battelle Columbus Laboratories, Columbus, Ohio 43201

■ Aliphatic alkanes and alkenes were irradiated with ultraviolet light ($\lambda \geq 2900Å$) in the liquid phase, in the presence of sulfur dioxide and oxygen. Both the hydrocarbon reactivity and the nature of products formed in solution show significant similarities to experiments which have been carried out involving aerosols under atmospheric conditions. However, studies in the former system are greatly facilitated by the superior yield of products. The mechanism of triplet sulfur dioxide quenching, to form photosulfoxidation products, is discussed.

It is widely recognized that atmospheric photoreactions of sulfur dioxide may adversely affect the environment (Renzetti and Doyle, 1960; Urone and Schroeder, 1969; Altshuller and Bufalini, 1971). The disappearance of sulfur dioxide and hydrocarbons from the atmosphere is the subject of increasing study, yet attempts to determine the photosulfoxidation products of atmospheric hydrocarbon pollutants have been unsuccessful (Renzetti and Doyle, 1960; Urone and Schroeder, 1969; Johnston and Dev Jain, 1960; Altshuller et al., 1968). However, the identification of such products in polluted atmospheres, or in environmental chamber simulations, is beset with a great number of difficulties, by far the greatest of which results from the almost total lack of knowledge regarding the sulfur dioxide photoproducts which may be present.

We have studied the photosulfoxidation of aliphatic hydrocarbons in the liquid phase, and have been able to identify the major reaction products by gas chromatography combined with mass spectral analyses (gc–ms) and infrared (ir) spectroscopy. Pure hydrocarbon was irradiated with a high-pressure mercury arc equipped with a filter which transmits wavelengths longer than 2900Å, while sulfur dioxide and oxygen were bubbled through the liquid at 22°C. From hydrocarbon reactivity (which was qualitatively assessed) and the nature of products formed, aliphatic alkanes and alkenes may be broadly separated into three groups: alkanes, terminal alkenes, internal alkenes. When similar experiments were carried out in the dark, the products reported below were not detected.

Alkanes

The major products are sulfonic acids, highly branched molecules being more reactive on account of the increased lability of tertiary and secondary C—H bonds. The free acids were methylated to facilitate analysis, all of the methyl sulfonates exhibited strong ir absorbance at approximately 7.35 μ, 8.5 μ, and 9.95 μ. The S—O—C stretch bands usually occurred between 12.0 μ and 13.5 μ, for example 12.78 μ for the *n*-octane product, and 12.5 μ and 13.05 μ for the isooctane product. From preliminary gc–ms [electron ionization (ei)] analyses we have tentatively identified the expected isomeric sulfonic acids in some instances, the photosulfoxidation (followed by methylation) of 2-methylbutane produces mainly methyl 2-methyl-2-butanesulfonate $[(M + 1)^+ = 167, (M - 29)^+ = 137]$, and some methyl 3-methyl-2-butanesulfonate $[(M + 1)^+ = 167, (M - 42)^+ = 124]$.

Internal Alkenes

Internal alkenes reacted more readily than either alkanes or terminal alkenes, and formed almost exclusively 1,3,2-dioxathiolane 2-oxides (cyclic sulfites), which has not previously been reported. The products from trans-2-butene, 2-methyl-2-butene, trans-2-pentene, and trans-3-heptene all show a characteristic ir absorption band at approximately 11.0 μ, other absorptions occurring at approximately 8.3 μ, 9.5 μ, and 13.3 μ. The mass spectrum [chemical ionization (ci) with methane] of the photosulfoxidation product from trans-2-pentene showed a prominent parent peak $[(M + 1)^+ = 151]$, and a peak corresponding to loss of sulfur dioxide, both being consistent with 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide. These analytical assignments were confirmed by comparison with 1,3,2-dioxathiolane 2-oxide (glycol sulfite, Aldrich Chemical Co.) and 4,5-dimethyl-1,3,2-dioxathiolane 2-oxide prepared from 2,3-butanediol (Breslow and Skolnick, 1966).

Terminal Alkenes

The reactivity of terminal alkenes is midway between those of alkanes and internal alkenes, the ir spectra of the products

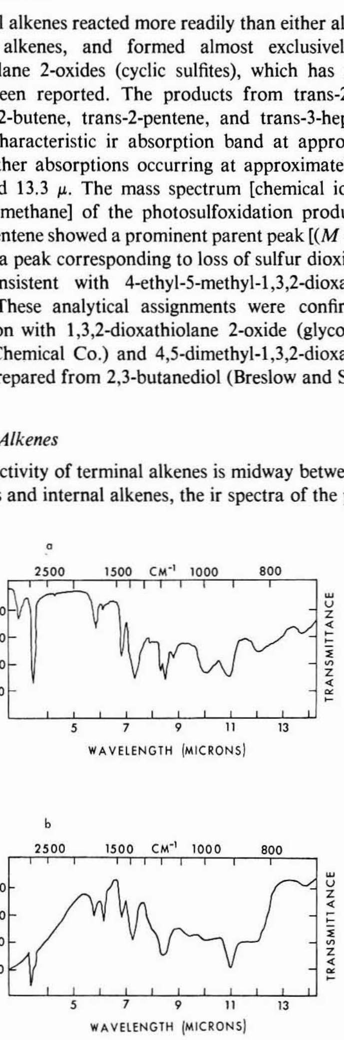

Figure 1. Ir analysis

a. **Photosulfoxidation products of 1-heptene in the liquid phase**
b. **Aerosol generated from an irradiated mixture of 1-heptene, sulfur dioxide, and NO_x**

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[1] To whom correspondence should be addressed.

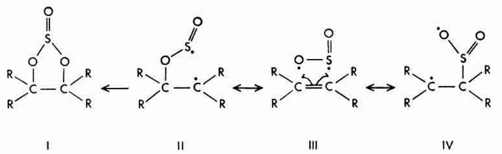

Figure 2. Mechanisms for quenching of triplet sulfur dioxide, and formation of cyclic sulfites from alkenes

suggest that both sulfonic acids and cyclic sulfites are formed, in addition to a carbonyl compound. Gc–ms analyses of the 2-methyl-1-butene methylated photosulfoxidation products are consistent with the formation of 2-methyl-1-butene-3-sulfonic acid [$(M + 1)^+ = 165$ (ci with methane)] and 2-formyl-2-butanesulfonic acid [$(M + 1)^+ = 181$, $(M - 31)^+ = 149$ (ei)]. Further studies are being carried out in an attempt to determine the factors influencing the formation of either 1,3,2-dioxathiolane 2-oxides or 2-formyl-2-alkanesulfonic acids.

Discussion and Mechanism

While liquid phase photosulfoxidation studies are interesting in their own right, the justification for carrying out these reactions as an aid to the identification of photoproducts under atmospheric conditions is that whenever we have made comparisons between the two systems, overwhelming similarities have been evident. Studies of the reactions of hydrocarbons and sulfur dioxide under simulated smog conditions have shown that sulfur dioxide consumption, hydrocarbon consumption, and aerosol formation are greatest for internal alkenes and least for alkanes (Renzetti and Doyle, 1960; Wilson and Levy, 1972; Prager et al., 1960). This is the same as the order of reactivity which we observe in the liquid phase reactions. It has been demonstrated that sulfur dioxide disappearance in smog conditions is greatest when the rate of formation of aerosol is maximum (Wilson and Levy, 1970). This may suggest that aerosol formation is in part caused by sulfur dioxide, but more significant is the disappearance of sulfur dioxide coincident with the appearance of a dispersed liquid phase. Thus the important reactions of sulfur dioxide may indeed occur in the liquid phase or at a gas/liquid interface. However, perhaps the most striking similarities, from the data available, have been apparent from comparison of the ir spectra of products from the two systems. The spectrum of the products from 1-heptene, sulfur dioxide, nitrogen oxides, and air in an environmental chamber under simulated atmospheric conditions (Wilson, 1972) shows significant similarities to our results from the liquid phase photosulfoxidation of 1-heptene (Figure 1*a*, *b*). Similarly, many of the major peaks in the ir spectrum (Wilson, 1972) of filtered auto exhaust (using sulfur-containing fuel) which is subsequently exposed to uv light, may tentatively be assigned to 1,3,2-dioxathiolane 2-oxides and sulfonic acids by comparison with ir spectra from liquid phase reactions.

We believe that the photosulfoxidation products from alkenes are formed as a consequence of reaction of an initial charge-transfer complex, and are dictated by the structure of the alkene under the given reaction conditions. The complex may absorb light resulting in a local triplet-excited state of sulfur dioxide, alternatively the complex may be formed upon quenching of the excited sulfur dioxide triplet by the hydrocarbon. In either case, triplet sulfur dioxide is the reactive species as has been pointed out by Calvert (Badock et al., 1971). The formation of such charge-transfer complexes, III (Figure 2), between sulfur dioxide and hydrocarbons has been established (De Maine, 1957; Andrews and Keefer, 1951; Nagai et al., 1966; Valyashko and Cheshka, 1953; Jones and Adelman, 1972). Of the two extreme intermediates, II is likely to have significantly greater stability in view of the higher strength of the C—O bond compared to the C—S bond. Furthermore, sulfur has a greater availability of suitable orbitals which facilitate radical stabilization.

We suggest that formation of high yields of 1,3,2-dioxathiolane 2-oxides from the photosulfoxidation of alkenes is a consequence of oxidation at the carbon radical of intermediate type II with molecular oxygen. This would ultimately lead to the formation of an alkoxy radical (not shown), whereupon ring closure would readily yield the cyclic sulfite, I. The formation of cyclic sulfites through IV is doubtful in view of the unfavorable entropy and enthalpy changes in the cyclization to a four-membered intermediate, in addition to the earlier considerations.

The proposed importance of II in cyclic sulfite formation is dissimilar to the views of Calvert and co-workers, who suggest that intermediate IV satisfactorily accounts for the observed photoreactions of sulfur dioxide and alkenes, based on their work in the gas phase (Badock et al., 1971). Similarly, the importance of II is apparent from studies of triplet sulfur dioxide quenching by carbon monoxide (Timmons, 1970), in which carbon dioxide is the major product. In this case product formation through intermediate type IV is impossible yet intermediate type II would readily cleave to yield carbon dioxide. Furthermore, the reaction of triplet sulfur dioxide with ethylene tetrafluoride (Cehelnik et al., 1971) to form CF_2O, CF_2, and SO may also be interpreted as proceeding through an intermediate of type II.

We are presently engaged in detailed studies of the products and rates of photosulfoxidation of several hydrocarbons, and hope to establish the operative mechanisms for individual cases.

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industry trends

Georgia-Pacific has placed a spanking new 20-acre ocean shipping facility for surplus wood chips in operation on the Portland, Ore. coast. The facility will handle wood chips from three states on their way to Japan and other timber-poor countries.

Combustion Equipment Assoc. has been awarded a $1.6 million contract by the city of Chicago for construction of four scrubbers to remove fly ash from stack gases of a 200-tpd municipal incinerator. Contract, on a turn-key basis, calls for recycling of scrubbing water.

Kaiser Engineers has received a $500,000 contract from the Atomic Energy Commission to study storage for radioactive wastes. Two-year study will evaluate use of specifically engineered facilities to contain wastes for a minimum of 100 years.

Mogul Corp. will be national sales distributor for Cutrine, a new algaecide developed by Applied Biochemists, Inc. Product is said to be superior to many copper-based algaecides in controlling planktonic, filamentous, or Chara-type growths.

Capital Controls Co. and Fischer & Porter Co. have been elected to associate membership in the Chlorine Institute, a nonprofit trade association dedicated to promoting safety in production, packaging, shipment, and use of chlorine.

Garret Research and Development, a subsidiary of Occidental Petroleum Co., has received a grant from EPA to study pyrolysis of industrial wastes for recovery of oil and activated carbon.

PPG Industries will begin construction of a liquid waste incinerator to destroy liquid organic sludge from the company's Delaware industrial coatings and automotive refinishes plant. The unit will burn about 100 gph and will operate on a self-fueling principle after wastes are ignited.

Combustion-Engineering's Canadian division has received a multimillion dollar contract from Calgary Power Ltd. (Calgary, Alta.) for construction of two 357-MW controlled circulation boilers. The boilers will be installed at units 3 and 4 of the utility's Sundance plant, located on the shore of Wabamun Lake, about 50 miles west of Edmonton.

Arthur D. Little Co. has received a $500,000 contract from the Coast Guard to develop a nationwide information system for accidental spills of hazardous materials transported over water. The Chemical Hazards Response Information System (CHRIS) will eventually be administered by the Coast Guard from its Washington, D.C. headquarters.

The Arizona Nuclear Power Project (ANPP) has selected NUS Corp. (Rockville, Md.) to conduct environmental studies for a nuclear power plant to be built in Arizona. ANPP is a joint venture of Arizona Public Service Co., Salt River Project, and Tucson Gas and Electric Co.

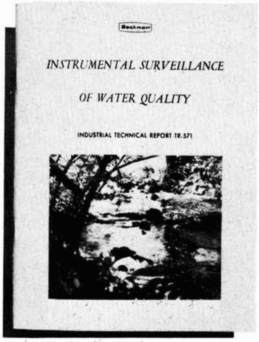
Firestone Tire and Rubber has completed a $5 million rubber processing system which provides automatic enclosed handling of carbon black during tire manufacture. The system will provide pollution-free dust control using dust collectors and scrubbers.

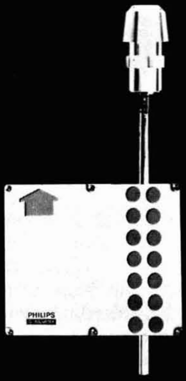
First Worth Corp. (Ft. Worth, Tex.) has received a $2 million contract for cooling tower modules to be installed for the New England Power Co., Summerset, Mass. An additional contract in excess of $1 million for a cooling tower system at Parque Central, a planned community in Caracas, Venezuela, was also announced.

Burns & Roe, Inc. will serve as an engineering consultant to Caltex Petroleum Corp. for an 800,000-gpd desalination plant at a refinery in the Persian Gulf.

Scott Research Laboratories (Plumsteadville, Pa.) has received a contract from EPA to develop technical specifications for standard gas mixtures for use in measurement of mobile source emissions.

United States Filter Corp. (New York, N.Y.) and the Slick Corp. have been merged, with U.S. Filter surviving as the parent company.

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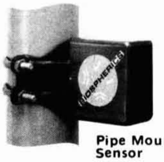
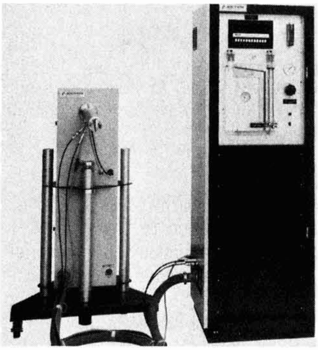

BIOSPHERICS
Pipe Mounted Sensor


BIOSPHERICS
Open Channel or Tank Sensor


Control Unit

new products



Sampler

Portable sampler employs an absorption refrigeration system with polyethylene sample container. Contains 12-lb pressurized gas source but can also be connected to external source of nitrogen or compressed air. Brandywine Valley Sales Co. 61

Particulate sampler

High-volume particulate sampler—rated at 7 ft^3/min—aids in measuring gaseous emissions and particulates from large stacks, incinerators, afterburners, and other combustion sources. System is compatible with all components of EPA-recommended particulate sampling train. Aerotherm/Acurex Corp. 62

Phosphate analyzer

Automated on-line phosphate analyzer can be used for total automatic closed-loop control of primary sewage influent. Used with appropriate control system, analyzer helps prevent occurrence of algal blooms. Ionics, Inc. 63

Screeners

Screeners use gyratory screening motion for waste water cleanup, solids recovery, and other pollution control applications. Models are available in over 100 standard types in aluminum, stainless or mild steel construction. Orville Simpson Co. 64

CO analyzer

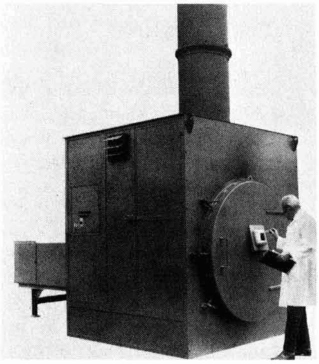
Portable analyzer used with company's Faristor cartridge sensors detects and measures carbon monoxide concentrations in stack and vehicular exhausts. Envirometrics, Inc. 65

CO detector

Detector is small card impregnated with chemicals which indicates normal, caution, or danger levels of CO. Also applicable to hydrogen sulfide measurement. Tomorrow's Products Co. 66

Reference PCB

Reference standard solution of polychlorinated biphenyls (PCB's) are supplied in septum top bottles for gas chromatography or other analytical applications. Concentrations of 10 or 100 ppm in benzene are supplied, with dilution accuracy better than 0.5%. Duke Standards Co. 67



Destructor

Controlled atmosphere destructors combust all types of organic waste while conforming to all state and federal air pollution requirements. Pyrolysis-type unit operates without scrubber and therefore needs no water supply or drainage site. Besser-Wasteco Corp. 68

Arsenic test kit

Kit detects presence of arsenic in polluted waters, effluents, or body fluids as well as other properly pretreated samples at levels of 30 ppb. Cost is about 75c/test. Koslow Scientific 69

Afterburner

DFS Fumebator is a packaged, direct-fired afterburner which can be incorporated into virtually any existing exhaust system to provide control of hydrocarbons or nondepository fumes and vapors. Air Purification Methods, Inc. 70

Reverse osmosis

Reverse osmosis system automatically and continuously reclaims textile lubricant for reuse. Other applications include reclamation and recycling of soluble, emulsified or infinitely suspended organic or inorganic material. Osmonics, Inc. 71

Lime handling

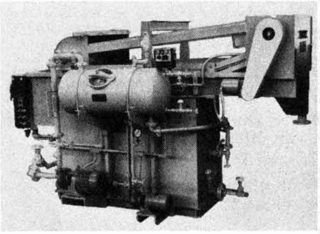
New line of lime-handling systems for industrial waste water treating operations can be purchased either as individual components or custom-engineered system. Carter-Day Co. 72

Mist filters

Hydrophobic filters are designed to control submicron aerosol emissions including inorganic "smokes," textile mill and plastic flooring plant emissions, and H_2SO_4 plant fumes. Cebeco Mgf. Co., Inc. 73

Ozone monitor

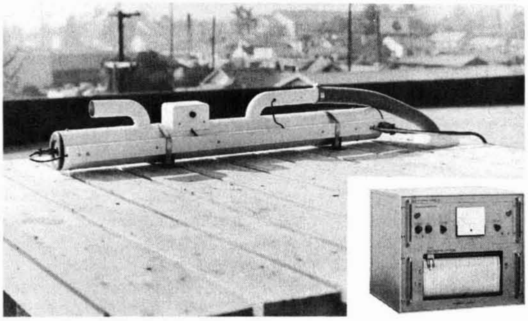
Monitor can detect ozone by chemiluminescence reaction and is designed to operate in unattended mode for periods up to 30 days. McMillan Electronics Corp. 74

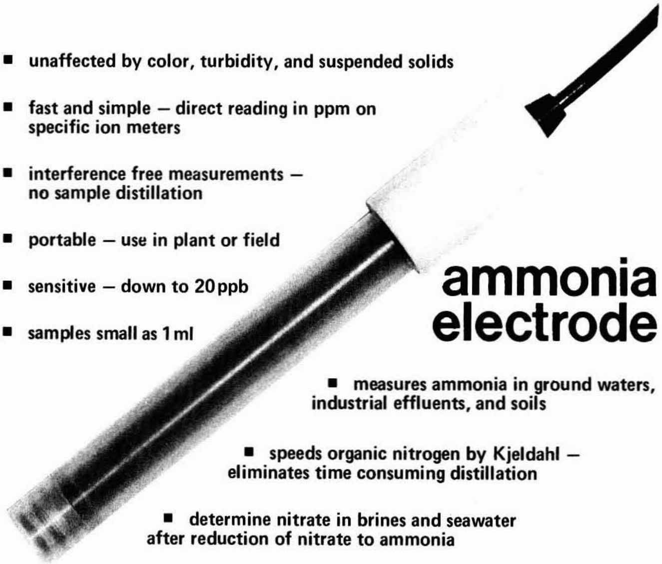


Waste water treatment

Waste water treatment systems for food and dairy industries are packaged units that use dissolved air flotation in a once-through operation to remove 85–90% of the fats and solids from a plant's effluent. Treatment capacities range from 10,000 to 1 million gpd. Komline-Sanderson Engineering Corp. 75

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.





Balance

High-speed electronic microbalance features four-place digital readout (no verniers). Balance has 5-gram capacity, 0.1-μg sensitivity and 10-mg electrical zero or tare. Sierra Instruments Corp. **76**

Clarifier

Unique liquid flow pattern of clarifier minimizes short circuiting and provides highest efficiencies at both design and peak flows. Lakeside Equipment Corp. **77**

Afterburner

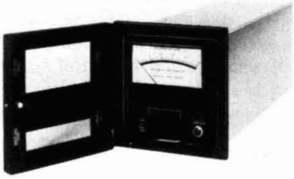
Turbomix afterburner, available in capacities from 1500 to 10,000 scfm, is designed for continuous duty operation at 1500°F. Unit can cut cleanup costs since up to 95% hydrocarbon destruction and odorless discharge are obtained at 1200°F instead of higher temperatures usually required. TEC Systems, Inc. **78**

Oil monitor

Sophisticated dual beam instrument detects oil concentrations as low as 1 ppm and warns of contamination before it becomes a problem. Detector can be used for monitoring plant discharges or refinery effluent and for protecting in-plant process streams and boiler condensate returns. Bull & Roberts, Inc. **79**

Sampler

New series of automatic samplers withdraws composite samples of liquids or slurries flowing through pipes, troughs or tanks. Some units are approved for sanitary sampling applications. Bristol Engineering Co. **80**



Temperature analyzer

Model 3500 temperature analyzer uses a stainless steel–encased, linear sensistor element for continuous monitoring of temperature in water quality studies. Weston and Stack, Inc. **81**

Air filter

High-performance filter is designed to clear dust-laden air at high air-to-cloth ratios. Uses air shock method to purge dust from replaceable cloth filter bags. Buhler Corp. **82**

new literature

Engineering manual. Manual will assist engineers in the proper sizing and selection of wet-scrubbing systems for industrial pollution control. Manual describes a wide range of scrubbing systems with proved industrial applicability. Koch Engineering Co., Inc. 91

Ir analyzers. Bulletin describes line of Luft-type infrared analyzers with various applications to pollution control and monitoring. Bulletin is illustrated with photographs and schematics of both standard and explosion-proof models. Mine Safety Appliances, Inc. 92

Drinking water. Bulletin classifies contaminants in drinking water and compares methods for removal. Emphasis is on reverse osmosis systems. Polymetrics, Inc. 93

Corrosion inhibitors. Bulletin 697 discusses use of condensate corrosion inhibitors to prevent corrosion in boiler condensate return lines, valve seats, and heater tubes. Also describes broad range of filming amines and neutralizing amine products to counteract effects of carbon dioxide, oxygen, and carbonic acid. Betz 94

Coagulants. Flyer describes two off-white, dry, high-molecular-weight anionic polyelectrolytes. Polymers are most effective when used as primary coagulant aids and flocculants. Calgon Corp. 95

Mass flowmeters. Catalog covers company's line of linear and nonlinear mass flowmeters, automatic flow controllers, and gas flow probes for stack gas velocity measurement. Teledyne Hastings-Raydist 96

Separator. Brochure entitled "Water, Waste and Sewage Treatment," discusses company's products related to treatment of industrial and municipal waste water. De Laval Separator Co. 97

Fabric filter. How company's fabric dust filters provide high performance with low initial installation and operating costs is subject of 8-page bulletin. Air Preheater Co. 98

Gas chromatographs. New 18-page bulletin describes two high-performance gas chromatographs which incorporate digital programmers, and direct-reading pneumatic controls. One model is especially suited for pollution control studies. Beckman Instruments, Inc. 99

Clarifiers. Brochure describes circular clarifiers, half- and full-bridge clarifiers, and square tank circular clarifiers with various mechanical options. Keene Corp. 100

Laboratory services. Brochure outlines analytical services to municipalities. Included are potable water testing, municipal waste analyses, and swimming pool water testing. Gilbert Associates, Inc. 101

Test papers. New edition of company's catalog lists more than a hundred indicator and test papers for pH, cation and anion detection, and numerous papers for determination of a wide range of substances. Gallard-Schlesinger Chemical Mfg. Corp. 102

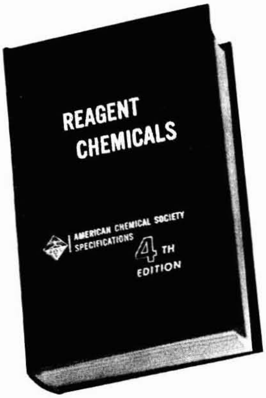
Foundry pollution. New product bulletin lists solutions for pollution problems in the foundry. Deals with such topics as noise control, vibration absorption, dust control, sand and casting cooling, and material handling. Rex Chainbelt, Inc. 103

Odor control. Bulletin contains on-site photographs and detailed drawings documenting applications of packed crossflow wet-scrubbing systems for odor abatement in fish meal reduction, poultry rendering, and pet food processing. Ceilcote Co. 104

Dust control. Brochure describes company's experience and capabilities in dust control and complete air cleanup systems. Includes brief case histories indicating company's successes in sanitary tissue, nonwovens, building material, asphalt, quarry, pharmaceutical and chemical fields. G. A. Kleissler Co. 105

Dairy wastes. Six case histories tell of company's successful efforts at cleaning up effluents from dairies. Smith & Loveless Div., Ecodyne Corp. 106

(Continued on p 940)



Stills. New 12-page catalog lists 240 combinations of water stills and accessories and gives detailed instructions on sizing still needs, heat sources, controls, etc. Barnstead Co. **107**

Engineering services. Bulletin 26-3 discusses the four broad areas of water pollution control expertise necessary for completion of any successful pollution control project and details company's capabilities in environmental engineering. Calgon Corp. **108**

Analytical services. An 8-page pamphlet describes company's activities in analysis and solution of waste water treatment problems. Company acts as a third party in negotiations between buyer and seller of pollution control equipment to provide objective assessment of treatment processes and monitor performance after installation. Commercial Testing & Engineering Co. **109**

DO meter catalog. New 4-page illustrated catalog lists company's line of portable DO and temperature-measuring instruments. Yellow Springs Instrument Co. **110**

Applications book. Comprehensive applications book tells how to get maximum use from company's BOD analyzer. Arthur Bros. Co., Inc. **111**

Shredder/compactor. Catalog describes specifications and applications of SHREDpactor refuse crusher. American Sterilizer Co. **112**

Thickener. Product literature describes company's CableTorQ thickener and clarifier design which allows unit to react automatically to heavy sludge conditions. Dorr-Oliver, Inc. **113**

Treatment Services. Bulletin tells of company's complete waste treatment services available to metal finish industry. Oxy Metal Finishing Corp. **114**

Periodical. "Millipore Technology" is free periodical dealing with areas of pollution control and public health. Millipore Corp., Bedford, Mass. 01730 (Write direct.)

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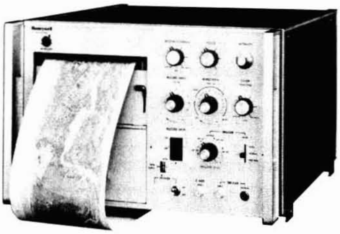

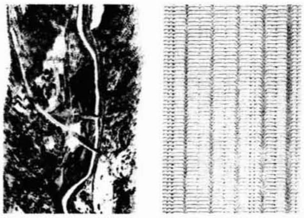

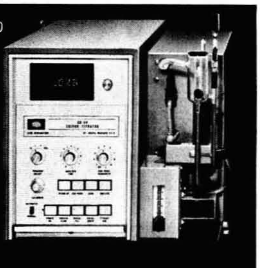

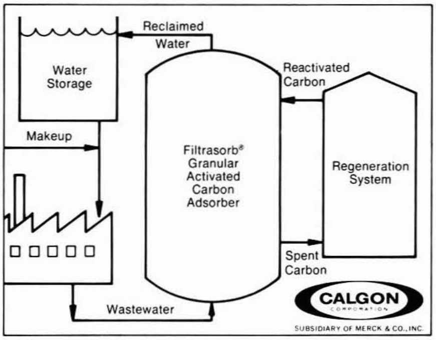
Reclaimed Water
Water Storage
Makeup
Filtrasorb® Granular Activated Carbon Adsorber
Reactivated Carbon
Regeneration System
Spent Carbon
Wastewater
CALGON CORPORATION
SUBSIDIARY OF MERCK & CO., INC.

bookshelf

The Susquehanna Compact: Guardian of the River's Future. William Voigt, Jr. x + 336 pages. Rutgers University Press, 30 College Ave., New Brunswick, N.J. 08903. 1972. $15, hard cover.

Covers the history of and describes the Susquehanna River Basin Compact. Shows how one important and complex piece of major legislation was passed by three individual state governing bodies and the federal Congress. Contains the full text of the Compact. ■

Ion Exchangers: Properties and Applications. Konrad Dorfner. 317 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1972. $17.50, hard cover.

In English for the first time, this volume is the enlarged and revised edition of a monograph on the properties and applications of ion exchanges. Previously available only in the original German. Intended for students, researchers, and industrial scientists. ■

Vehicle Emissions Measurement—Panel Discussion. R. F. Knudsen, Ed. i + 20 pages. Instrument Society of America, 400 Stanwix St., Pittsburgh, Pa. 15222. 1972. $4.00, paper.

Contains six papers and question-answer session examining measurement and testing problems associated with reducing vehicle emissions. Papers cover the overall problem, history and background, assembly-line emission testing, compliance testing measurement problems, New Jersey emission testing, and instrumentation for service garages. ■

Air Pollution and Its Control, 2nd Ed. Wayne T. Sproull. 132 pages. Exposition Press Inc., 50 Jerico Trnpk., Jerico, N.Y. 11753. 1972. $6.00, hard cover.

Sproull explains what air pollution is, how it endangers health, the cost of controlling it, what is being done about it now, and what should be done about it. Contains updated data in layman's language. Intended for laymen trying to make sense of a complex problem, for the technical minded, city planners, public officials, citizens' committees, and others actively working with air pollution. ■

Modern Hydrology. Raphael G. Kazmann. 2nd ed. xvii + 365 pages. Harper & Row Publishers, 49 E. 33 St., New York, N.Y. 10016. 1972. $14.95, hard cover.

Up-to-date reference work written in textbook style. Intended for scientists, engineers, industrialists, regulatory agencies, and concerned people generally. Author attempts to bring into focus the methodology and science of hydrology and the practical applications that have resulted. ■

Introduction to Environmental Science. Phillips W. Foster. xi + 181 pages. Learning Systems Co., 1818 Ridge Rd., Homewood, Ill. 60430. 1972. $3.50, paper.

Written in programmed learning format to provide the reader with a quick, efficient, and effective means of grasping the subject matter. Examines the relationships between man and his environment. Material can be used in virtually any ecology course, although it particularly fits in well with an introductory course in environmental science or ecology. ■

Man and the Environment. Harry N. M. Winten, Ed. xxi + 305 pages. R. R. Bowker Co., 1180 Avenue of the Americas, New York, N.Y. 10036. 1972. $12.50, hard cover.

A bibliography of selected publications of the United Nations system 1946–1971. Aim of the book is to call attention to generally valuable kinds of information and publications emanating from the international agencies of the United Nations. ■

Development and Environment. x + 225 pages. Co-Libri, P.O. Box 482, Hague 2076, Netherlands. 1972. $6.50, paper.

Report and working papers of a panel of experts convened by the Secretary-General of the United Nations Conference on the Human Environment. Conference held in Founex, Switzerland in 1971. Purpose of the conference: to convince the poorer nations that environmental problems facing richer nations are their problems also. ■

World Facts and Trends. John McHale. vii + 95 pages. Macmillan Co., 866 Third Ave., New York, N.Y. 10022. 1972. $2.95, paper.

Uses graphs, charts, and statistics, as well as text to demonstrate man's actual and potential capabilities to interfere with the natural environment. A study of man and the biosphere, environ systems, human systems, and indicators of change patterns. ■

Recycle This Book! J. David Allan, Arthur J. Hanson, Eds. xiv + 245 pages. Wadsworth Publishing Co., Inc., Belmont, Calif. 94002. 1972. $2.95, paper.

Represents the ideas of leading environmentalists in the nation and the viewpoints of students and professionals at the University of Michigan. Anthology of a cross section of viewpoints on environmental problems and their solutions. Based on materials from 1970 "teach-in" on the environment at the University of Michigan. ■

The Science of the Total Environment, Vol. 1. No. 1. E. I. Hamilton, Ed. 115 pages. Elsevier/North Holland, 335 Jan Van Galenstraat, P.O. Box 211, Amsterdam-W, Netherlands. 1972. $29.50 per volume of four.

Journal deals with all aspects of man's perturbations of the environment, their interrelationships, and implications for life. Covers air and water pollution, thermal pollution effects and heat reuse, solid waste disposal and reuse, noise, light, and electromagnetic interferences. ■

Treatment and Management of Urban Solid Waste. David Gordon Wilson, Ed. xiv + 210 pages. Technomic Publishing Co., Inc., 265 W. State St., Westport, Conn. 06880. 1972. $20, paper.

Provides information on planning, management, economics, techniques, and equipment to deal with such problems as urban refuse collection and street cleaning, quantitative estimates of solid waste, operations research and solid waste collection, landfill, municipal incineration, reclamation, composting, and waste management in buildings. ■

meeting guide

October 24–26

Engineers Society of Western Pa.

33rd International Water Conference

Pittsburgh, Pa.

Write: W. M. Porter, Secretary, Engineers Society of Western Pennsylvania, William Penn Hotel, Pittsburgh, Pa. 15219

October 24–28

Federation of Societies for Paint Technology

50th Annual Meeting

Atlantic City, N.J.

Includes topics on air pollution control, water pollution control, and solid waste disposal. Contact: Federation of Societies for Paint Technology, 121 S. Broad St., Philadelphia, Pa. 19107

October 25–26

New York State Action for Clean Air Committee

Eighth Annual Symposium on the Environment and Health

Syracuse, N.Y.

Theme "Environmental Education for the Adult Public." Write: New York State Action for Clean Air Committee, 105 E. 22nd St., New York, N.Y. 10010

October 25–28

Clackamas Community College

Environmental Technology Show

Oregon City, Ore.

Will focus on new technological equipment and research. For information: Marvin Weiss, Community Services Office, 19600 S. Molalla Ave., Oregon City, Ore. 97045

October 29–November 3

American Society of Agronomy and others

64th Annual Meeting

Miami Beach, Fla.

Theme for the meetings "Serving Man in an Urban Environment." Contact: American Society of Agronomy, 677 S. Segoe Rd., Madison, Wis. 53711

October 30

Wilks Scientific Corp.

Ambient Air Measurement Seminar

Atlantic City, N.J.

Featured as part of this year's Eastern Analytical Symposium. Contact: Carol Kaplin, Seminar Coordinator, Wilks Scientific Corp., P.O. Box 449, South Norwalk, Conn. 06856

October 30–31

American Society for Mechanical Engineers and others

Joint Engineering Management Conference

Atlanta, Ga.

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

October 30–November 1

Technical Assoc. of the Pulp & Paper Industry and Canadian Pulp & Paper Assoc.

1972 International Sulfite & Recovery Conference

Boston, Mass.

Discussions include recovery and pollution control techniques. Write: TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

October 30–November 2

American Water Resources Association

Eighth Annual American Water Resources Conference

St. Louis, Mo.

General theme concerned with the engineering, social, environmental, and political interactions that occur in the formulation, design, construction, and operation of large-scale water resource projects. Contact: American Water Resources Association, P.O. Box 434, Urbana, Ill. 61801

October 30–November 3

Canadian Council of Resource and Environment Ministers

Man and Resources National Workshop

Montebello, Que.

Purpose is to establish guidelines for best relationship between man and environment. Write: Canadian Council of Resources & Environment Ministers, 1170 Beaver Hall Sq., Montreal 111, P.Q., Canada

October 31–November 1

Purdue University

11th Annual Air Pollution Control Conference

Lafayette, Ind.

Contact: David W. Hawkins, Civil Engineering Bldg., Purdue Univ., Lafayette, Ind. 47907

October 31–November 2

U.S. EPA, National Science Foundation, and Columbus Laboratories of Battelle

Environmental Resources Conference

Columbus, Ohio

Will focus on sources of trace metals in the environment, transport and effects, control processes, monitoring, and legal and economic aspects of pollution. Write: G. Ray Smithson, Jr., or Duane Yothers, Columbus Laboratories of Battelle, 505 King Ave., Columbus, Ohio 43201

November 6–7

U.S. EPA and Univ. of Georgia

Applications of Mass Spectrometry to Environmental Problems Symposium

Athens, Ga.

Will deal with present and potential uses of mass spectrometry for identifying and measuring organic and inorganic pollutants. Write: Ann Alford, Southeast Water Laboratory, EPA, College Station Rd., Athens, Ga. 30601

November 8–9

Process Equipment Manufacturers Association

PEMA Fall Meeting

Chicago, Ill.

Also Wastewater Equipment Council Meeting. Contact: Art Parchen, Executive Director, P.O. Box 8745, Kansas City, Mo. 64114

November 13–15

University of Texas at Austin

Specialty Conference: Applications of Commercial Oxygen to Water and Wastewater Systems

Austin, Tex.

For more information: Richard E. Speece, 305 Engineering Labs Bldg., Univ. of Texas, Austin, Tex. 78712

November 14–16

Ariz., Colo., and N.M. Air Pollution Control Programs

North American Conference on Motor Vehicle Emissions Control

Albuquerque, N.M.

Conference will investigate improvements in public transportation systems, traffic restraints, land use control, and other topics. Contact: Rowene C. Danbom, Public Relations Officer, Colorado Dept. of Health, 4210 E. 11th Ave., Denver, Colo. 80220

November 16–17

University of Alberta

Symposium on Lakes of Western Canada

Edmonton, Alta., Canada

Will cover lake management problems. Contact: The Water Resources Centre, Box 5000, The University of Alberta, Edmonton, Alta. T6G 2H1

November 26–30

American Institute of Chemical Engineers

65th Annual Meeting

New York, N.Y.

Includes symposium on trace contaminants in the environment. Write: AIChE, 345 E. 47th St., New York, N.Y. 10017

November 26–30

American Society of Mechanical Engineers

1972 Winter Annual Meeting

New York, N.Y.

Includes Energy Crisis Forum. Write: Maurice Jones, ASME, 345 E. 47th St., New York, N.Y. 10017

(Continued on p 944)

December 4-7
Clapp & Poliak, Inc.
International Pollution Engineering Congress & Exposition
Cleveland, Ohio
Sessions related to users of pollution control equipment and products. Contact: Clapp & Poliak, Inc., 245 Park Ave., New York, N.Y. 10017

December 4-7
American Geophysical Union
Fall Annual Meeting
San Francisco, Calif.
Contact: American Geophysical Union, 2100 Pennsylvania Ave., N.W., Washington, D.C. 20037

December 6-8
IEEE, AEC, and NASA
1972 Nuclear Science Symposium
Miami Beach, Fla.
Includes environmental research and monitoring. Write: W. W. Managan, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Ill. 60439 or H. A. Thomas, Golf Energy and Environmental Systems, P.O. Box 608, San Diego, Calif. 92112

December 11-14
International Assoc. of Hydrologic Sciences and others
International Symposium on Uncertainties in Hydrologic and Water Resource Systems
Tucson, Ariz.
Includes interface between water resource management/society/nature/man. Write: Chester C. Kisiel, Chairman, Organizing Committee, International Symposium, Dept. of Hydrology and Water Resources, 208 East—Old Psychology Bldg., Univ. of Arizona, Tucson, Ariz. 85721

December 18-22
Florida Technological University
American Association of Professors in Sanitary Engineering Workshop
Orlando, Fla.
Topic is mathematical modeling in environmental engineering. Write: Marty Wanielista, Director, Environmental Systems Engineering Institute, Florida Technological University, P.O. Box 25000, Orlando, Fla. 32816

January 18-19
Northwestern University and American Chemical Society
39th Annual Chemical Engineering Symposium
Rosemont, Ill.
Theme "Environmental Impacts of Chemical Engineering." Contact: Jean Kovalcik, The Technicological Institute, Northwestern University, Evanston, Ill. 60201

January 22-26
Highway Research Board
52nd Annual Meeting
Washington, D.C.
Contact: Hugh Gillespie, Public Information Officer, Highway Research Board, 2101 Constitution Ave., Washington, D.C. 20418

January 27-February 1
National Asphalt Pavement Assoc.
18th Annual Convention
Miami Beach, Fla.
Covers environmental control and other topics. National Asphalt Pavement Assoc., 6811 Kenilworth Ave., Riverdale, Md. 20840

Courses

October 19-20
University of Wisconsin
Recycling Municipal Wood Fiber Wastes for Paper Manufacture Short Course
Milwaukee, Wis.
Fee: $95. Write: University of Wisconsin—Extension, Dept. of Engineering, 600 W. Kilbourn Ave., Milwaukee, Wis. 53203

October 20-November 21
University of Rochester
Insights into Engineering Course
Rochester, N.Y.
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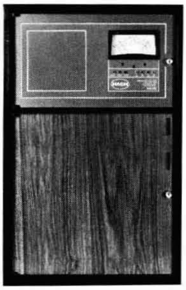

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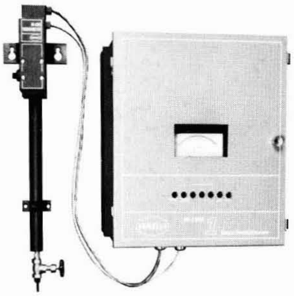

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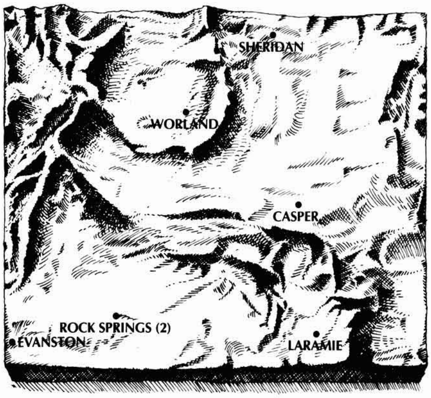
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